DESIGN AND OPTIMIZATION OF SURFACTANT BASED ENHANCED REMEDIATION OF BUNKER C FUEL OIL CONTAMINATED SOIL

By

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ABSTRACT

Soil pollution, particularly by petroleum compounds is a very important global issue. It is typically a result of improper storage and disposal, historic careless spills, accidental spills, and leaks from tanks. This environmental damage can result in wide spread groundwater and surface water contamination, and limit soil use for agricultural purposes. There are a large number of brownfield sites across Canada. These are sites that have been previously used for industrial and commercial activities and have been contaminated with hazardous wastes. Newfoundland and Labrador (NL) in particular, has numerous sites due to a legacy of fuel oil use for power generation at abandoned, old and emerging mining fields. Data from the federal contaminated site inventory indicate that on federal owned sites in NL, there are over 3000 m^3 of oil-contaminated soil. It has therefore become necessary to develop remediation technologies that are economically and technically feasible, environmentally friendly, fast, and applicable in a wide range of physical settings.

A wide range of technologies have been developed over the past few decades for the remediation of contaminated sites. Some of these processes have been found to be successful in removing only a specific group of contaminants from the soil. As a result, combinations of different approaches are usually adopted for more effective remediation thereby leading to more expensive remedial operations. Surfactant-enhanced remediation technology, otherwise known as soil washing has proven to be

an effective method to remove a mixture of contaminants such as heavy metals, petroleum compounds, volatile organic compounds, pesticides and herbicides as well as other hazardous and non-degradable substances from contaminated soils. Surfactant remediation relies on the ability of surfactant formulations to remove both organic and inorganic contaminants from soil and sediments by desorbing them from the solid to liquid phase. The technology removes contaminants via two mechanisms; one occurs below the Critical micelle concentration (CMC) of the surfactants known as mobilization mechanism, and the other above the CMC known as solubilization mechanism. However, this technology has not been widely reported for the remediation of Bunker C fuel oil, a complex and recalcitrant petroleum compound that is persistent in the environment and extensively reported to be resistant to chemical and biological degradation, and therefore difficult to remediate.

This research presents an assessment of the performance of soil washing technology for the remediation of Bunker C contaminated oil from weathered contaminated soil using patented surfactant formulations. Weathered soil are known to be more difficult to remediate than freshly contaminated soil hence, the study used weathered soil in order to be certain of the effects of soil washing on Bunker C removal. Specific research objectives include: (1) determining the micellar properties (Surface Tension and CMC) of the patented surfactants, (2) development of a reliable analytical method for the analysis of (heavy) petroleum hydrocarbons in soil, (3) evaluation of the parameters that govern the implementation of soil washing and an assessment of their effects on the

washing of weathered Bunker C oil from contaminated soil at surfactants concentrations below the CMC (mobilization mechanism) using the multivariate experimental and statistical approach, (4) determination of the optimum conditions (optimization) for the removal of Bunker C oil with the tested surfactants.

The research, in the course of analysing the Total Petroleum Hydrocarbon in the soil using the Canada-Wide Standard (CWS) for Petroleum Hydrocarbon in soil is used for the analysis of petroleum hydrocarbon compounds found considerable variability and inconsistencies in the results. This could be due, in part, to the different gas chromatography (GC) conditions, soil properties, as well as and other steps involved in the method. These differences impacts the determination of the effectiveness of remediation at hydrocarbon-contaminated sites. The thesis therefore, developed validated the analytical method for the quantitative analysis of TPH in (contaminated) soil. The newly developed method was successfully applied for a faster and more reliable analysis of TPH of Bunker C oil in contaminated soil.

It is expected that this research will lay a road map for further studies on the application, optimization and development of a treatment system protocol for the use of soil washing for Bunker C remediation. It should be noted that although Bunker C is the contaminant, the hydrocarbon composition of Bunker C makes it a good surrogate for other heavy oils.

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LIST OF ABBREVIATIONS AND SYMBOLS

ANOVA	Analysis of Variance
BBD	Box-Behnken Design
CCME	Canadian Council of Ministers for Environment
CCD	Central Composite Design
CDS	Chromatographic Data System
CE-UV	Capillary Electrophoresis - UV detection
CMC	Critical Micelle Concentrations
CWS	Canada Wide Standard
DNAPL	Dense Non Aqueous Phase Liquid
FFD	Fractional factorial Design
FID	Flame Ionization Detector
FFD	Full Factorial Design
GC	Gas Chromatography
GC-MS	Mass Spectrometry
GFF	General Factorial Design
HOC	Hydrophobic Organic Compound
HPLC	High Performance Liquid Chromatography
ITOPFL	International Tanker Owners Pollution Federation Limited
ITC	Isothermal Titration Calorimetry
LNAP	Light Non Aqueous Phase Liquid

MEKC	Micellar Electro-kinetic Chromatography
MS	Mass Spectrometry
MUN	Memorial University of Newfoundland
N.D	Non Detected/No Detection
NMR	Nuclear Magnetic Resonance
P and T	Pump and Treat
PAH	Polycyclic Aromatic Hydrocarbons
PCB	Polychlorinated biphenyl
PBD	Plackett-Burman Design
RSD	Response Surface Design
RSD	Relative Standard Deviation
SESW	Surfactant Enhanced Soil Washing
STDV	Standard Deviation
SOx	Sulphur Oxides
SVE	Soil Vapor Extraction
TOC	Total Organic Carbon
TPH	Total Petroleum Hydrocarbon
USEPA	United States Environmental Protection Agency

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CHAPTER ONE

INTRODUCTION AND OVERVIEW

1.1 PREAMBLE

The increasing demand to meet the energy and resource needs have led to increased industrial activities, and as a result, large areas of lands have been contaminated by petroleum hydrocarbon and derivative products. This problem is particularly relevant in countries such as Canada, due to resource based economy and resulting in exploration, production, and processing activities related to resource development resulting in a large number of oil-contaminated sites. Hydrocarbon compounds travel kilometers away from point of spills through porous soils under the influence of gravity and capillary forces.

A contaminated soil is one which its characteristics have been modified by the presence of a hazardous substance, with a concentration such that could be considered a risk to human health and the environment [1]. Hydrocarbons are one of the most common agents of soil contamination. They are organic compounds consisting of carbon and hydrogen atoms, mostly from fossil fuels [2]. They exhibit low biodegradability and high toxicity and can therefore persist in the environment for years and even decades. The release of oil due to accidental spills and leaks from (underground) storage tanks have been the major sources of pollution of soil and the environment. Improper storage,

handling, disposal, pipeline corrosion as well as blow-out from pipes and pumps [3], and everyday operations at retail outlets [4] have also been identified as sources of petroleum hydrocarbons in the soil. In most cases, intentional discharge of oil and oily wastes to water and land could be a major cause of this environmental damage [5]. The most common hydrocarbon contaminants include; crude oil, gasoline, diesel, polychlorinated biphenyls (PCBs), polyaromatic hydrocarbons (PAH), Bunker C, engine oil, etc. Among these commonly encountered hydrocarbons in the environment, Bunker C fuel oil, also known as fuel no. 6 [6] or Bunker C fuel oil [7], come across as one of the most recalcitrant hydrocarbon compounds that is difficult to remediate [8].

According to the International Tanker Owners Pollution Federation Limited (ITOPFL) [9], over 1.1 million tonnes of oil is estimated to have spilled worldwide in the last decade, and in 2013 alone, three major oil spills of international standard occurred with over 700 tonnes or more oil spilled, with one incident accounting for the vast majority of the total. In Canada, data from the federal contaminated site inventory indicate that there are over 30,000 m^3 of brownfield sites across Canada [10]. These are sites that have been previously used for industrial and commercial activities and have been widely contaminated with hazardous wastes. It is estimated that over $40 billion dollars will be required to clean up the nearly 22,000 contaminated sites across the country, and there is currently an on-going 15 year plan to execute these remediation projects in phases [11]. Therefore, soil pollution by hydrocarbon is a major problem across the world.

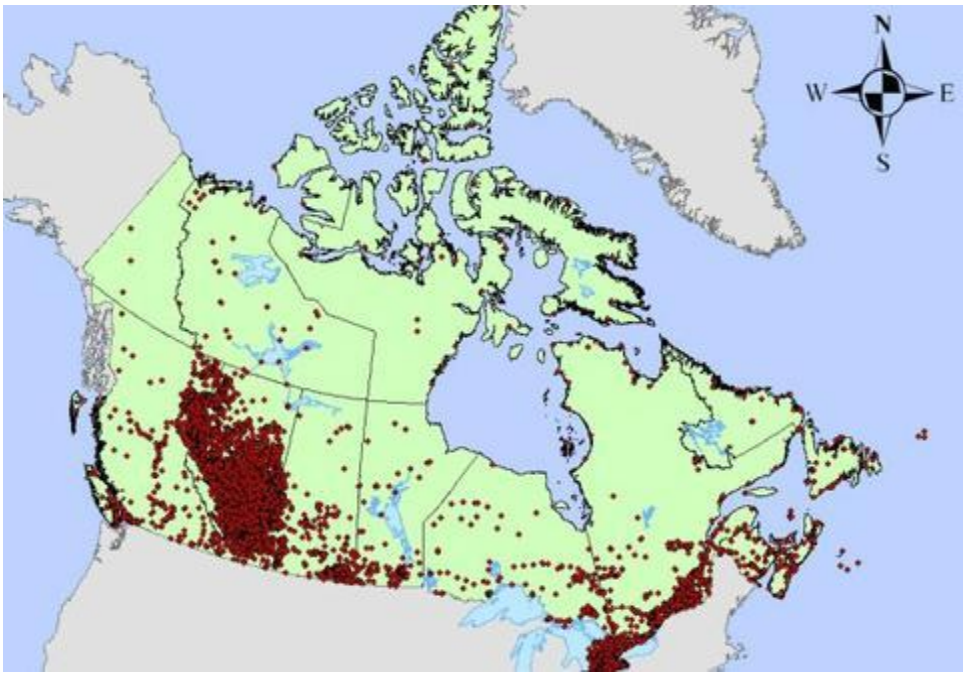

Figure 1.1 Contaminated Sites across Canada
Source: Suzy Thompson [11]

The last decades have witnessed the development of many remediation technologies for the recovery, re-use and restoration of sites impacted by hydrocarbon compounds. These include; soil vapor extraction (SVE) [12-16]; land farming [16-20]; soil flushing [16, 21-23]; solidification and stabilization [12, 16, 18]; thermal desorption [15, 16, 24]; phytoremediation [16, 25-29]; bioremediation [30-34]; bioventing [16, 35-37]; encapsulation [16, 38, 39]; and soil washing [40-48]. Some of these processes have been found to be successful for removal of a specific group of contaminants from the soil. As a result, one or more approaches are usually combined for more effective treatment resulting in expensive remedial operations [49]. Site characteristics, regulatory requirements, cost and time constraints [18, 50] are factors which determines the

selection of a suitable remediation technology. A particular contaminated site may also require a combination of procedures and processes to allow the optimum remediation for the prevailing conditions [16].

Surfactant-enhanced remediation technology; simply known as '*Soil Washing'*, has proven to be an effective method to remove a mixture of contaminants such as heavy metals, petroleum compounds, volatile organic compounds, pesticides and herbicides as well as other hazardous and non-degradable substances from contaminated soils and water in a one step process. The technology utilizes the desorption and solubilization characteristics of surfactant compounds in removing contaminants from the surfaces of soil and sediments and transferring these contaminants into the liquid phase [51]. It is easy to implement, efficient, economical and environmentally friendly [52]. The process is cost effective, relatively fast, and has the potential to treat and recover large volumes of contaminants [53].

1.2 PROBLEMS AND MOTIVATION FOR THE RESEARCH

The mining industry is a vital economic sector for the people and the government of Newfoundland and Labrador (NL). The industry employs about 2500 people, and accounts for 8 % of the Gross Domestic Product (GDP) of the provincial goods [54]. Petroleum hydrocarbon compounds released into the environment as a result of mining activities are of particular interest. NL has numerous sites due to a legacy of fuel oil use for power generation at abandoned, old and emerging mining fields. Recently, soil

contaminated with Bunker C oil was found during the reconstruction phase of a former mine in Newfoundland. Evidence shows that Bunker C storage tank had leaked at the site since early 1980's. Bunker C oil is known to be very resistant to most of the popular remediation technologies. It is composed of complex chemical constituents and regarded as one of the most difficult compounds to clean-up. It therefore, became imperative to find an effective and economically feasible remediation option to clean up the site.

Soil Washing has been widely appraised as an effective remediation technology for cleaning up a variety of contaminants and mixture of contaminants from the soil and water, which can be used for both in-situ and ex-situ remediation [55]. In spite of the enormous amount of reported studies on the remediation of petroleum hydrocarbon compounds and other hazardous contaminants using soil washing, soil washing for the remediation of Bunker C contaminated soil has not been widely and extensively investigated. Contaminants such as; crude oil, engine oil, gasoline, diesel etc. [56-61], heavy metals [45, 46, 49, 62-64], PCBs [41, 65, 66], wood preservatives [67], PAH [66, 68, 69], phenanthrene [70], pesticides [71, 72] and a mixture of contaminants [49] have been successfully remediated using soil washing. It is also worth noting that this technology has been widely adopted in cleaning up superfund sites in the USA [73]. However, it has not been widely investigated for maximum Bunker C remediation from the soil, nor has the behavior and reactions of surfactants during surfactant soil washing with Bunker C oil been documented.

1.3 RESEARCH OBJECTIVES AND SCOPE

This research studied the use of non-ionic surfactants for remediation of the weathered Bunker C contaminated soil under different washing conditions. Emphasis was placed on washing at concentrations below the critical micelle concentration (CMC) in order to verify the occurrence, and the ability of the mobilization mechanism to efficiently remove Bunker C from contaminated soil. Weathered soils are more difficult to remediate, as weathering processes such as evaporation and degradation concentrate contaminants with higher molecular weight, viscosity and density, as well as enhances the binding strength of oil to soil [69, 74]. Mass transfer rates of hydrophobic organic compounds (HOCs) are also known to be small in weathered soils [75], therefore, weathered contaminated soils, which is the focus of this study, are usually much more difficult to remediate than recently contaminated soils [32]. The (physical and chemical) properties of the weathered, field contaminated soil will be determined prior to the commencement of the soil washing experiments.

The specific objective is to screen, identify, and evaluate the effects of soil washing and the environmental parameters that could govern the implementation of soil washing technology for weathered Bunker C remediation under different conditions. Previous researches on soil washing have highlighted the variation in the performance and reaction of different surfactants to different experimental factors. Therefore, the research would focus on utilizing fractional factorial experimental design minimum

number of experiments to identify the effects of the selected experimental parameters on each of the tested surfactants on the overall Bunker C removal efficiency.

The research also intended find the optimum operating the conditions (optimization) for achieving maximum Bunker C removal.

Iveysol® surfactants, a Canadian proprietary surfactant formulations manufactured by Iveysol® International Inc., and which has been used for the remediation of different hydrocarbon contaminants in high-profile remediation projects across Canada [51, 52, 76-84] will be used for this study. This study intends to use these surfactants because they are fast becoming household name in the Canadian environmental remediation industry. Our findings showed that, the surfactants have not been well characterized with respect to their surface-active properties especially, their surface tension and CMCs. This study will attempt to determine the CMC of Iveysol® 106 and 108 surfactant formulations through two different methods, namely; the Tensiometer and the Pendant Drop techniques, before further utilizing them for soil washing of Bunker C.

To adequately quantify the amount (concentration) of Bunker C oil resident in the soil prior to soil washing and the percentage removed due to the effects of the soil washing, it is very important to have a reliable, reproducible and robust analytical method. The reference method for the Canada-Wide Standard (CWS) for Petroleum Hydrocarbon in soil, used for the analysis of petroleum hydrocarbon compounds across Canada has often shown considerable variability in the results. This study will use multivariate

experimental design approach to develop, optimize and validate a more robust CWS method for total petroleum hydrocarbon (TPH) analysis in the soil, for a more reliable TPH analysis. More specifically, the study will determine the optimum gas chromatography (GC) operational settings and conditions for not only Bunker C, but the analysis of other heavy oils in the soil.

The scope of this research includes:

1. Accurately determine the surface tension and critical micelle concentration (CMC) of the surfactants (previously unavailable in the literature).
2. Characterize the physiochemical properties of the soil, i.e. particle size analyses, pH, bulk density, conductivity etc.
3. Develop a method for the analysis of petroleum hydrocarbon in the soil and validate the method. The existing method has a number of limitations which has prevented the development of effective remediation processes.
4. Evaluate the effects of washing parameters on Bunker C removal with each surfactant and identify the significant parameters for each surfactant.
5. Identify the difference, if any, in the behavior and reaction of the non-ionic surfactants with Bunker C oil.
6. Study the interaction of washing parameters in relation to Bunker C removal with each surfactant.

7. Use numerical optimization and predictive approach to determine the optimum Bunker C removal condition for each surfactant, and conduct experiments to validate the predicted optimal parameters for Bunker C soil removal.

It is expected that this study will lay a road map for further research on the application, optimization and development of a treatment system protocol for the use of SESW for Bunker C remediation. It should be noted that although Bunker C is the contaminant, the hydrocarbon composition of Bunker C, being the heaviest of all fuel oils, and its other constituents, makes it a good surrogate for other heavy oils.

1.4 OVERVIEW ON BUNKER C FUEL OIL

Bunker C also known as fuel oil no. 6 [6] or Bunker C fuel oil [85], is a complex petroleum mixture derived from residuals of refining processes [8]. It is the heaviest of all fuel oils [8], and contains high concentrations of *n*-C_{12} through *n*-C_{34} alkanes [86] and appreciable quantities of polycyclic aromatic hydrocarbons (PAHs), with concentrations of four to six ring condensed PAHs representing 5 % or more of the total mass [6]. Furthermore, According to Tang et al [87] Bunker C oil contains elevated levels of sulfur (1.5 – 4.0 wt.%). It also contains asphaltenes, which has an extremely complex structure and high molecular weight [88]. These high fraction of heavy hydrocarbons and other complicated constituents translates to a low water solubility (complicating removal by water based treatment processes), low volatility (limiting thermal treatment), and low

biodegradability (resistance to microbial breakdown), leading to its continued persistence in the environment.

Bunker C is widely used around the world, which makes it a very common pollutant. In Singapore, for example, the supply of Bunker C oil to marine vessels is a multi-billion dollar industry [89]. It is one of the most commonly used forms of marine fuel for shipping [87, 90], and also used in oil fired power generation, and at remote site locations like mine sites [40]. Bunker C is regarded as one of the most frequently spilled petroleum products in the US [8] and known to be more toxic than other petroleum oils because of its high PAH content [90].

1.4.1 Environmental Fate and Effects of Bunker C Pollution

The release of petroleum oil (hydrocarbon) into the environment is an important stressor to the sensitive (natural) ecosystem [91]. Bunker C contamination, due to its complex chemical composition [8, 87], weathers slowly when spilled, and can persist relatively unchanged for years [90, 92]. The ecological effects of Bunker C spillage are enormous. Ingestion of low concentrations of this oil product is associated with reproductive failure [93], genotoxicity [94], and hematological changes [95, 96] in different animals. Environmentally, its elevated sulfur content generates serious air pollution during combustion due to SOx emission [97], while its PAHs content makes it a potential cancer causing contaminant, because many PAHs are carcinogens [98] and immunotoxins [99].

1.4.2 Remediation of Bunker C Oil

Over the past years, concerted efforts have been geared towards the remediation of Bunker C from the soil with the use of well-known remedial processes, most of which have been reported to be unsuccessful by many researchers. Song *et al.,* [31], studied the microbial degradation of terrestrial fuels (gasoline, jet fuel, heating oil, diesel oil and Bunker C) in different soils. The research reported that degradation of Bunker C from the soil was very slow and incomplete, as none of the Bunker C treated soils reached a 50 % reduction after 48 weeks of treatment. According to their results, bioremediation initially accelerated Bunker C degradation, but no further stimulation was recorded after 8 weeks. The study suggested that Bunker C components are structurally resistant to biodegradation, and concluded that bioremediation has only very limited beneficial effects on Bunker C remediation from the soil. These results confirmed the findings of Walker *et al.,* [100], which had earlier reported Bunker C to be the least susceptible oil to biodegradation in a study where biodegradation of two crude and two fuel oils were compared.

Richmond *et al.*, [8], experimented the optimization of emulsification and biodegradability of Bunker C oil from the soil obtained from the sandy oiled beach near Dutch harbor, Alaska. They reported an 8 % mineralization of Bunker C after 6 weeks of treatment, and also noted the toxicity of the oil to the microbes. In another research, Floodgate [101] stated that when Bunker C spills, its high viscosity leads to the formation of tar balls, that can physically isolate a bulk of the oil from microbial

degradation and dispersion. The tarry consistency of Bunker C [6] makes it difficult to be remediated from the contaminated surfaces, while a report of a study on oil spill case history conducted by the National Oceanic and Atmospheric Administration (NOAA) [102] stated that Bunker C is difficult to remove from oiled surfaces, and relatively recalcitrant to biodegradation [8]. It is also reported to be the least susceptible fuel oil to biodegradation [100]. Bunker C weathers very slowly, chemical dispersion is seldom effective, and clean-up is difficult under all conditions [102].

From the foregoing, it can be concluded that current remediation strategies are inadequate and a need exists for research aimed at improving our ability to clean-up past and future spills of Bunker C [8].

1.5 Overview on Surfactants

A surfactant is a substance that, when present at low concentration in a system, has the property of adsorbing onto the surfaces or interfaces of the system and altering the surface or interfacial free energies of those surfaces or interfaces [103]. They are molecules capable of associating to form *micelles*; which is an aggregate of surfactant molecules or ions in solution [104]. They are the active ingredients found in soaps and detergents, and are commonly used to separate oily materials from a particular media [42].

Structurally, surfactants have a characteristic molecular structure consisting of a functional group that has no affinity for liquids known as *lyophobic or hydrophobic group,* and another group that has strong attractions for liquids known as *lyophilic or hydrophilic group.* The combination of these dual groups in one chemical is why surfactants are structurally described as *amphiphatic* in nature. Surfactants are often diagrammatically represented with the head and tail group model as shown in Figure 1.2. *The hydrophobic group*s are oil soluble and are always the alkyl hydrocarbon groups of C_nH_{2n+1}-, C_nH_{2n-1}-, C_nH_{2n+1}-, etc., whilst the *hydrophilic group* which are water soluble include -COO-Na^+, -SO4 -Na^+, -SO3 Na^+, -OH^-, etc. [105].

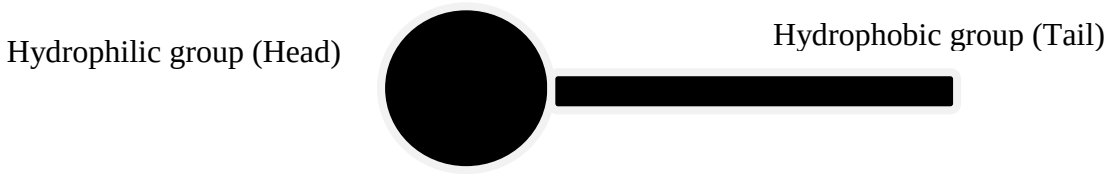

Figure 1.2 Surfactants head and tail model
Source: Urum [105]

Surfactants can be classified into four groups, based on the nature of their hydrophilic (head) groups. Namely: anionic, cationic, non-ionic and zwitterionic surfactants [103]. They can also be classified into Biosurfactants and Chemical (synthetic) surfactants respectively, based on their mode of origin [106].

1.5.1 Classification of Surfactants

Depending on the nature of the hydrophilic (head) group, surfactants are classified as [103]:

1. *Anionic*: Their surface-active portion of the molecules bearing a negative charge, e.g. $RCOO^-Na^+$ (soap), $RC_6H_4SO_3^-Na^+$ (alkylbenzene sulfonate) etc. These surfactants are best used on positively charged surfaces, i.e. if the surface is to be made *hydrophilic* (water-wettable).

2. *Cationic*: Their surface active-active portion bears a positive charge e.g. $RNH_3^+Cl^-$ (salt of a long chain amine), $RN(CH_3)_3^+Cl^-$ (quaternary ammonium chloride). If a negatively charged surface is to be made *hydrophobic* (water repellant) by use of a surfactant, cationic surfactants are best used. They will adsorb onto the surface with their positively charged *hydrophilic* head group oriented toward the negatively charged surface because of electrostatic attraction.

3. *Zwitterionic*: Both positive and negative charges may be present in the surface-active portion. For example, $RN^+H_2CH_2COO^-$ (long-chain amino acid), $RN+(CH_3)_2CH_2CH_2SO_3^-$ (Sulfobetaine). Since this class of surfactants carries both positive and negative charges, they can adsorb on both negatively and positively charged surfaces without changing the charge of the surface significantly.

4. *Nonionic*: The surface-active portion bears no apparent ionic charge, e.g. $RCOOCH_2CHOHCHOH$ (monoglyceride of long-chain fatty acid), $R(OC_2H_4)xOH$ (polyoxyethylenated alcohol) etc. This group of surfactants adsorb onto surfaces with either *the hydrophilic* or *hydrophobic* group oriented toward the surface,

depending upon the nature of the surface. If polar groups capable of H bonding with the *hydrophilic* group of the surfactant are present on the surface, then the surfactant will probably be adsorbed with its *hydrophilic* group oriented towards the surface, making the surface more *hydrophobic.* If such groups are absent from the surface, then the surfactant will probably be oriented with its hydrophobic group toward the surface, making it more *hydrophilic.*

Based on their origin, surfactants can also be classified as [106]:

1. *Biosurfactants*: These are surfactants produced from biological-based materials [105] or simply microbes. They are amphiphilic, structurally diverse compounds of microbial origin, mainly produced by hydrocarbon-utilizing microorganisms which exhibit surface activity [107]. Biosurfactants are mainly produced by bacteria or yeast, and also available from plants, animals and including human [106]. They both biodegradable, and non-toxic or less toxic than chemical surfactants. Some common biosurfactants include; Aescin, Rhamnolipid, Lechitin etc.
2. *Synthetic Surfactants*: These are surfactants produced from chemically based materials. Most of the commercially available surfactants are chemical surfactants, mainly petroleum-derived [107]. A group of synthetic surfactants have recently received considerable attention. They are surfactants whose molecules contain more than one hydrophobic tails and hydrophilic heads. These

surfactants are called *gemini* surfactants or twin surfactants or *dimeric* surfactants [106].

1.5.2 Critical Micelle Concentration

At low concentrations surfactants exist solely as *monomers*. These monomers will accumulate at interfaces present in the system (e.g., air-water, oil-water, soil-water etc.). As the interfacial areas are satisfied and the aqueous surfactant concentration increases the monomers aggregate to form *micelles* as shown in Figure 1.3. The concentration at which micelles first begin to form is known as the *'Critical Micelle Concentration* (CMC)*'* [108]. The CMC does not only determine a number of interfacial phenomena, such as detergency, solubilization etc., but also affects other phenomena such as surface or interfacial reduction, that do not directly involve micelles [103].

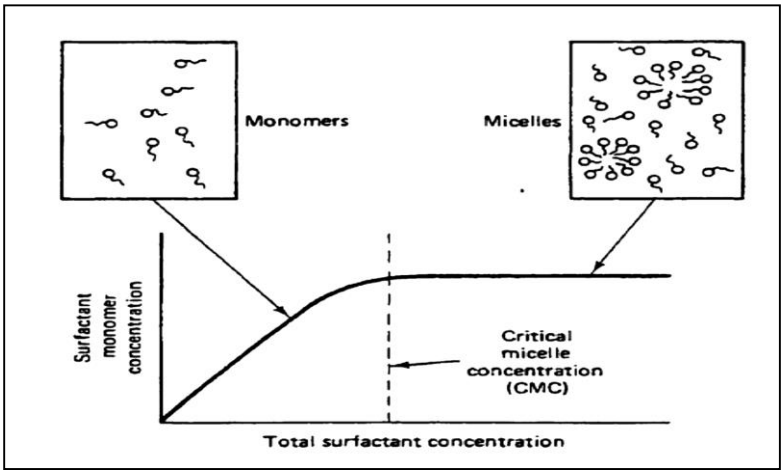

Figure 1.3 Formation of micelles at Critical Micelle Concentration
Source: Zhao [109]

The physiochemical properties of surfactants vary markedly above and below the CMC value [104]. The CMC values are also important in virtually all of the industrial surfactant applications. They can enhance the apparent solubility of Hydrophobic Organic Compounds (HOCs), below or the above CMC, in the remediation of contaminated soils and sediments [110] in the environmental industry; and a number of enhanced or improved oil recovery processes involving the use of surfactants are achieved when a significant concentration of micelles are present [104].

1.5.3 Solubilization

Solubilization is one important surfactant property that is directly related to micelle formation. It is the spontaneous dissolution of a substance (solid, liquid or gas) by irreversible interaction with the micelles of a surfactant in a solvent to form a thermodynamically isotropic solution with reduced thermodynamic activity [103]. The aqueous solubility of oil is the apparent solubilization due to the brining together of volume of oil and water to equilibrium, then analyzing the water rich phase for oil content [105]. The ability of surfactants' to remove oil from contaminated media can be evaluated through the rate of solubilization of single or double components of petroleum hydrocarbon components [111].

If the solubility of a normally solvent-insoluble material is plotted against the concentration of the surfactant that is solubilizing it, the solubility will be very low until the CMC is reached. Then the solubility of the solvent-insoluble material will increase

linearly with the concentration of the surfactant [103]. At concentrations above the CMC level, surfactants have the ability of solubilize more of hydrophobic organic compounds than would be dissolve in water alone

1.5.4 Fate and Behavior of Surfactants on the Soil

When soil is exposed to a considerable quantity of surfactant, even at low concentrations, surfactants seem to alter significantly the chemistry, physics and biology of the soil [112]. Nearly all surfactant properties and processes are of potential significance in understanding the behavior of surfactants and HOCs in a soil/aqueous system, but surfactant sorption onto soil is a particularly important process [113]. Sorption of surfactant onto the soil may result in the surfactant being unavailable for micellar solubilization of HOCs [114], and may result in the loss and reduction of their concentration, limiting the effectiveness in soil treatment [105]. The sorption of surfactants can also influence biodegradation activities in the soil [115]. In addition, the presence of sorbed as well as dissolved surfactant changes HOC sorption behavior [114, 116]. Surfactant sorption on soil however, depends on the pH, ionic strength, and organic carbon content of the soil [112].

According to Haigh [117], cationic surfactants tend to adsorb strongly onto clays and colloidal materials as well as onto organic matter. Adsorption of cationic surfactants to soil surfaces is extensive. Anionic surfactants on the other hand, tend to adsorb or bind

less strongly. The adsorption of non-ionic surfactants, as with other non-polar compounds, is influenced mainly by the organic carbon content of the soil.

With regards to degradation of surfactants in the soil, the anionic LAS and non-ionic LAE surfactants are degrade rapidly in sludge-amended soil and even in soils with no previous exposure to the materials [117]. The product of microbial degradation of surfactants may be relatively toxic, as is the case for alkylphenol ethoxylates [118], or relatively non-toxic, as is the case for aikyl ethoxylates [119].

Kuhnt [120] did an elaborate review on the fate, behavior and reaction of surfactants in the soil and their effects on soil processes. Some of the key processes described include surfactant sorption, degradation and the ability of surfactants to modify the soil structure, surface characteristics and wettability.

1.6 SOIL REMEDIATION TECHNOLOGIES

Different advanced remediation technologies have been developed in recent years. Most of these technologies have been found to be effective to certain extent, in remediating most of the widely encountered contaminants in the soil. These soil treatment technologies can been classified into four main categories [105, 121], namely:

- Chemical/physical treatment methods
- Biological treatment methods
- Thermal treatment methods
- Off-gas treatment technologies

The processes employed by these technologies include isolation, immobilization, toxicity reduction, physical separation and extraction. These approaches can be used for many types of contaminants but the specific technology selected for contaminated soil will depend on the type and form of contamination, and other site specific characteristics [122]. In remediating hydrocarbon impacted soil, one or more of these approaches are combined for more effective treatment. The process of reducing the petroleum constituents present in the soil by spreading the soils on the ground and stimulating aerobic microbial activity within the soils through aeration and/or the addition of nutrients, minerals, and water/moisture known as *"Landfarming"* is only effective in remediating lighter petroleum hydrocarbons [16, 19, 123], as heavier hydrocarbon do not evaporate or microbially degrade through this process [16].

Solidification/stabilization, also referred to as *waste fixation*, is a remediation technology that reduces the mobility of oil and hazardous substances in the environment through both physical and chemical means [16, 37, 105]. This technology is not effective with organics [37], as they generally remain immobilized [124]. The innovative technology of heating contaminated soil at high temperatures (100 - 600 ^{o}C) to release petroleum hydrocarbon from the soil, (*thermal desorption*), although, effective for hydrocarbon contaminated soil, but it is expensive, environmentally unsafe because it generates emissions, and greatly affected by the presence of water in the soil [16, 105]. Another commonly used treatment process for hydrocarbon contaminated soil is "*Biopiles"*. It is a method that involves the piling of petroleum-contaminated soils

into piles or heaps and then simulating aerobic microbial activity by aeration and the addition of minerals, nutrients, and moisture [125]. The biopiled soils are often subjected to heat and pH alteration to enhance biodegradation [16]. This method is similar to *Landfarming*, but in the latter, the soil is aerated through tilling and ploughing [125]. This treatment option, is only effective in reducing light fractions of petroleum hydrocarbon in the soil [123], and does not also lead to complete removal or degradation of hydrocarbon from the soil [16].

Phytoremediation is a treatment method that uses plants to clean up hydrocarbon and other contaminants from the soil. The process takes advantage of the ability of plants to take up, accumulate, and/or degrade constituents that are present in soil or process them for physiological processes [16, 27]. This process is time consuming, as the remediation may require more than one growing season; and the treatment is limited to soils less than one meter from the surface [16].

Based on the limitations of the aforementioned popular remediation/treatment methods and the submission of various authors based on the failures of most of the well-known technologies for Bunker C clean-up in the soil, this research presents surfactant enhanced soil washing (SESW) commonly known as Soil washing.

1.7 SURFACTANT ENHANCED SOIL WASHING

Surfactant enhanced soil washing (SESW) simply known as "*Soil Washing"* is a soil treatment method classified as both chemical and physical treatment technology category [105]. The process involves high energy contact between the contaminated soils and an aqueous based washing solution, resulting in the separation of hazardous materials and/or the chemical transformation of contaminants into non-hazardous, unregulated substances [49]. It primarily utilizes liquids, usually water, occasionally combined with solvents i.e. surfactants, and mechanical processes to scrub soils [16].

Soil washing has been extensively used in remediating all kinds of hazardous contaminants from the soil. The literature revealed that soil washing using surfactants was actually developed for soils contaminated with petroleum hydrocarbons [55]. The technology has been studied and used on a large scale for remediation of hydrocarbon contaminated soil in Europe [126, 127], and for remediating "Superfund Sites" contaminated by hydrocarbon by-products in the U.S.A [73]. The development of this technology is largely a consequence of the failure of other remediation technologies to remove non-aqueous phase liquids (NAPLs) or sorbed contaminants from the surface and subsurface. When hydrophobic organic compounds (HOCs) such as petroleum products are adsorbed on a soil grain, it is difficult to remove them from the surface because HOCs are hydrophobic, hence they repel the liquids and chemicals from their surface and they have inherent low water solubility. Adding surfactants can loosen the HOC from the surface of the soil matrix and suspend it in the water phase. Once desorbed, the suspended HOC is more *'hydraulically-available'* for Pump and Treat (P

and T), more '*bio-available'* to the microbial population present (bioremediation), and more '*chemically available'* for oxidation or reduction reactions (chemical oxidation). In short, once liberated from the soil matrix, the HOC is more available for treatment by most, if not all forms of *in-situ* and *ex-situ* remediation treatment technologies [83].

This treatment, which can be used both in-situ and ex-situ [55] primarily uses surfactants as agents that desorbs the contaminants into the liquid phase. Vazquez *et al.* [1] reviewed sites where Soil washing has been used for both *in-situ* and *ex-situ*. These include sites contaminated with hydrocarbons, metals, or pesticides. All these are substances that tend to easily adhere physically or chemically to silt and clay and therefore are difficult to separate from soil containing high amounts of fine particles [128].

1.7.1 Mechanisms of Surfactant Enhanced Soil Washing

Soil Washing is governed by two distinct mechanisms, namely: '*Mobilization and Solubilization*" [74, 108]. These controlling mechanisms are dependent on the CMC of the surfactant. The Mobilization Mechanism or Soil Roll-up Mechanism [108] is a two-step process which occurs at concentration below the CMC. In the first step, surfactant monomers accumulate at the soil-contaminant and soil-water interfaces and increase the contact angle between the soil and the contaminant (i.e. alter the wettability of the system). Surfactant molecules adsorbed on the surface of the contaminant cause repulsion between the head group of the surfactant molecule and the soil particles,

thereby promoting the separation of the contaminant from the soil particles. In the second step, convective currents create agitation and abrasion which provides the necessary energy to create additional surface area of the oil phase and thus displace the oil from the soil.

The second mechanism is the *Solubilization Mechanism,* which takes place at concentrations above the CMC. Surfactant enhanced solubilization results from contaminant partitioning into the hydrophobic core of surfactant micelles. As the number of micelles in solution increases, solubilization also increases. Thus, concentrations well above the CMC are necessary for this mechanism [108].

Surfactant enhanced washing below the CMC (mobilization mechanism) have been highlighted in many studies for not only being effective in remediating many contaminants in the soil and water [129, 130]; but also reduces the overall cost of remediation. It is also very compatible with analytical testing procedures used to measure the effluent [52]. Washing at higher surfactant concentration, apart from increasing the cost of remediation, is not beneficial due to colloid mobilization [131], clay swelling [132], and macroemulsion formation [133].

1.7.2 Factors Affecting the Efficiency of Surfactant Enhanced Soil Washing

The factors that affect the efficiency of soil washing are soil, contaminant and surfactant dependent. One of the notable soil factors is the type of soil to be treated. The

effectiveness of soil washing; according to the U.S EPA reports [127, 134], is dependent on the soil and contaminant type. The reports elucidated that the applicability of this procedure must be tested when the soils are classified as silt or clay because soil washing is not considered effective when soils contain more than 20 – 30 % silt/clay.

Clay content of the soil is a significant factor in soil washing. This is because, interfacial tension of the surfactant and clay will decrease surfactant concentration [55], thereby reducing the mobilization or solubilization efficiency of the surfactant. Gatchett and Bernejee [135]; emphasized the role of soil particle size and Total Organic Carbon (TOC) in the soil on the successful application of SESW. They argued that soils containing sand and other coarse materials are generally the most ideal for soil washing treatment. Soil containing large amounts of silt, clay, and humic substances, and soils with high total organic carbon (TOC) content are not treated as effectively by soil washing technologies. Another property of the soil that plays a significant role in determining the efficiency of soil washing is the permeability of the soil. Highly permeable soil gives more removal efficiency [136].

In summary, soil washing efficiency is related to soil characteristics and more specifically, information on grain size distribution, physiochemical properties, soil moisture content, soil organic material content, cationic exchange capacity and soil permeability [55] are important as they all affect soil washing. Remediation of soils contaminated with oil products with lower contaminant concentrations and larger

particle sizes, in same conditions, gives better removal efficiency than soils with higher contaminant concentrations and smaller particle sizes [55]. The solubility of the contaminants in water is another important factor that may affect the effectiveness of soil washing [136].

The type and selection of surfactants is another significant factor of consideration. In their study, Deshpande *et al* [108] highlighted the importance of surfactant selection in ensuring the success of soil washing. The study evaluated eight different ionic and non-ionic surfactants for enhanced soil washing of three different soils contaminated with petroleum hydrocarbon. The study concluded that when selecting a surfactant for a given soil-contaminant system, it is important to evaluate the surfactants at concentrations above and below their CMC, to ascertain the mechanism suitable for the surfactant and the contaminant under review.

1.7.3 Process Modeling of Surfactant Enhanced Soil Washing

While it is necessary to evaluate surfactants to be selected for soil washing [108], it is also very imperative to understand the partitioning of hydrophobic organic compounds (HOCs) within the soil-water-surfactant systems, as this is a key to improving the use of surfactant for remediation [137]. Many publications have provided insights into modeling of the distribution of HOCs between soil and water phases in the presence of surfactant micelles. Others have also been able to describe the mechanism of the

surfactant-aided soil washing system, with mathematical models to predict soil washing performance at various surfactant concentrations [72].

Mobilization and solubilization mechanisms govern the use of surfactants for remediation at surfactant concentrations below and above the CMC. However, much attention has been paid to modeling the solubilization of the HOCs, than the mobilization. Other areas have that have been widely modeled is the sorption of surfactants [138-140] to the soil. It is generally believed that as monomers (below the CMC), surfactants can only sorb onto solid surfaces [139]. This sorption of surfactants onto soils results in surfactant loss and reduced performance for the solubilization of HOCs.

Earlier studies on modeling of surfactant solubilization of HOC [141], had reported that the solubilization power of surfactant above the CMC for a given solute (contaminant) is expressed in terms of the molar solubilization ratio, rather than the partition coefficient between the micellar phase and the water. Wayt and Wilson [142] and Diallo et al. [143] reported that provided the CMC is reached, the concentration of the hydrophobic contaminants solubilized in surfactant solutions is a linear function of the total surfactant concentration.

In predicting the concentration of pollutants in the environment, various types of partition coefficients, such as Octanol-water partition coefficients (K_{ow}), K_{oc} and water solubility, have been used in different studies, from which the solubility can be

determined. For example, Jafvert [144] correlated the values of a micelle-water partition coefficient (K_m) with K_{ow} for a series of PAH compounds in dodecylsulfate (surfactant) micelles and found a near-unity slope and near zero intercept, which suggests the similarity of solvation energies for these compounds in micelles.

Many researchers [72, 114, 116] have examined the partitioning of HOCs in different phases of the surfactant-soil system. Chu and Chan [72] stated that the distribution of HOC and the solution phases of water and surfactants can be described by the distribution coefficient, $K_{d,}$

$$Kd = \frac{[P]Soil}{[P]w + [P]mic} \quad (1)$$

Where $[P]_{soil}$ is the pollutant concentration in the soil phase, $[P]_w$ is the pollutant concentration in water, and $[P]_{mic}$ dissolved in surfactant the micelles. The K_d value can be measured in the lab oratory, and be used as an index to quantify the efficiency of a surfactant-aided soil washing system [145]. For a better examination of the soil washing performance, Equation (1) can be re-arranged by taking its reciprocal;

$$\frac{1}{Kd} = \frac{[P]w}{[P]Soil} + \frac{[P]mic}{[P]Soil} \quad (2)$$

Where $\frac{1}{Kd}$ is the performance indicator of soil washing in terms of the fraction of the pollutant being solubilized in the liquid phase over the pollutant that remained in the soil phase after the soil washing process.

However, some researchers [104, 146] proposed that there could be some contaminants (NAPL) which may not be chemically associated with the soil, and instead coexists with the soil (in the subsurface), especially in the cases of accidental spills with heavy pollution. In this case, the NAPL is likely to be another major source (or the third phase) other than the soil contaminant in the soil and liquid phases [68]. The conclusion was that no matter the kind of HOCs involved, there are two main sources of HOC in the soil system before the washing is initiated. One is the fixed compound that is physically or chemically adsorbed or bonded in the soil media, and another is the free NAPL in the liquid phase. A finding, which was suspected by Boyd and Sun in 1990 [147].

The residual contaminant/NAPL in the system after the soil washing will exist in the aqueous phase and will be detected in the soil washing effluent. Based on these, they gave a more general expression of washing performance, $1/K_d$ which encompasses all possible sources of pollutants as shown in Equation (3) below:

$$\frac{1}{K\mathrm{d}} = \frac{[P]w + [P]mic + [P]NAPL}{[P]Soil} \qquad (3)$$

Where $[P]_{NAPL}$ is the pollutant in the NAPL form that exists in the liquid phase.

Applying this equation to model the performance of surfactants in soil washing system, Chu and Chan [72] noted that that the performance curves of the HOCs exponentially increased with the surfactant concentration and proposed a mathematical model to correlate the soil washing performance curves for HOCs.

Most of the previous literature surveyed focused on HOCs removal via micellization, i.e. solubilization mechanism at surfactant concentration above the CMC. The equations used in modeling and partitioning (such as those stated above) all have components e.g. $[P]mic$ which reflects surfactants concentration above the CMC. This might due to the general assumption that HOCs, which are generally insoluble in water, can only be desorbed or solubilized into liquid phase from the solid phase through the solubilization effects of surfactants when used at concentrations above their CMCs. A lot of authors are of the opinion that solubilization of HOCs is generally initiated at the CMC and is proportional to the bulk solution surfactant concentration beyond this point, which could be described by a micelle-water partition coefficient [145]. Only few studies like that of Kile and Chiou [141] take into account, the possibility of solubilizing HOCs by surfactant monomers (mobilization). They proposed a model to account for solubility enhancement due to both micelles and monomers. The study reported that, although the solubilities of the HOCs tested were greatly enhanced by all surfactants above the CMC, significant solubilities were enhanced below the CMC of certain surfactants. They suggested that solubility correlated better to the length of the hydrocarbon chain and accessibility to the inner core than to micellar size.

1.7.4 Advantages of Surfactant Enhanced Soil Washing

Surfactant-enhanced remediation technology has extensive applications for varied waste groups [49] and a mixture of contaminants such as heavy metals, petroleum

compounds, volatile organic compounds, pesticides and herbicides as well as other hazardous and non-degradable substances from contaminated soils, sludges and sediments [40]. The technology has a shorter treatment time when compared to bioremediation, phyotoremediation, and other biological methods which unlike soil washing, are largely affected by climatic factors [55, 57].

Soil washing has also been appraised to be cost effective, with potential to treat, reduce and recover large volumes of contaminants [49, 53, 55, 62]. The approach of soil washing prevents the generation of harmful by-products that may be produced during remediation processes and the application of surfactants will further reduce the risk associated with waste streams, as their (surfactant's) release will not damage the environment due to their inherent biodegradability and low toxicity [53]. While several methods of soil remediation examined at the laboratory scale were not applicable for field scale usage, soil washing has been used for many contaminants in both laboratory experiments and on commercial field scales [55, 148].

1.7.5 Challenges with Surfactant Enhanced Soil Washing

Despite the numerous benefits SESW has over other remediation technologies, there are certain challenges associated with its implementation in remediating contaminated soil. On a commercial (ex-situ) basis, contaminated soils are treated by excavating them from the site and transferred to another place to be washed. Darban et al. [55]

mentioned that, the cost of transportation could be high, and transporting the contaminated soil through residential zones could cause some health and environmental issues.

Several potential problems were identified concerning the use of aqueous surfactant solutions to clean contaminated soil. According to Abdul and Gibson [41], one of the challenges was identified was that surfactant itself should be environmentally safe, in that it should not be toxic or hazardous, and it should be easily removed from the subsurface by anthropogenic or natural processes. They stated further that, because of the surface-active properties of surfactants, they could disperse soil-clay particles; this could lead to clogging of the soil pore space and to the diversion of the surfactant solution from the contaminated zone. Therefore, it is expected that surfactant washing could present difficulties in applying, containing, and recovering the surfactant(s).

Retention of organic contaminants on coarser soil fractions and aquifer material after soil washing is another challenge posed by soil washing. This may be influenced by several factors other than particle surface area, including the hydrophobicity of the contaminant, the properties of the washing medium, and the characteristics of the soil particles [47].

Studies in the United States have also demonstrated that each soil requires a separate evaluation because considerable variations may occur in the effectiveness of the washing process [149]. Depending upon target treatment levels, the soil fractions

obtained during soil washing may require additional treatment to meet the total petroleum hydrocarbons (TPH) criteria for ultimate disposal [4].

On a commercial scale, the management, storage and treatment of the wastewater, containing the surfactant and the desorbed contaminant, generated after the washing, could be a serious and expensive challenge, as the washed water (effluent) requires further treatment before it can be disposed [16].

1.8 THESIS ORGANIZATION

This thesis consists of a series of manuscripts either submitted for review, revised for publication or in the process of being submitted for publication to reputable journals. Chapter two expatiates on the significance of the critical micelle concentration (CMC) as an important micellar property and highlighted various methods that can be used to determine this important phenomenon. The chapter further gave detailed information on the laboratory experiments done to determine the CMC of the Iveysol® surfactants with two different methods; the Pendant Drop and the Tensiometer techniques.

Chapter three focuses on the development and validation of a modified version of the Canada Council of Ministers of Environment's (CCME) standard for hydrocarbon analysis in the soil using Gas-chromatography Flame Ionization Detector (GC-FID), otherwise known as the Canada Wide Standard (CWS) method, which is the approved method for the assessment and remediation of contaminated sites in Canada. The study highlighted

the weaknesses of the existing CWS method which became apparent during the course of analyzing the Total Petroleum Hydrocarbon contained in the Bunker C contaminated soil, and how various researchers in the past had also reported discrepancies in some other analytical methods, which they sought to correct and improve. The chapter is divided into four sequential phases in a series of laboratory experiments that involved the use of Fractional factorial (fFD) to screen six (6) gas chromatographic factors, and subsequently optimizing the identified significant factors using a Central Composite Response Surface Design (CCD). The optimized conditions were further tested for robustness and a model was developed and validated by calibrating the GC system with a hydrocarbon standard using the optimized GC settings. The final phase of the the paper touched on the application of the optimized experimental conditions for the analysis of real hydrocarbon (Bunker C oil) sample.

Chapter four is a comprehensive study done to assess the efficiency of soil washing technology in remediating Bunker oil from (weathered) soil. The chapter includes a brief results of the preliminary soil analyses done to investigate the physical and chemical properties of the soil, a series of two-level fractional factorial designed experiments done to investigate the effects of the selected washing parameters on Bunker C removal, and how these factors interacts and can be combined for a successful Bunker C remediation. The data generated from the factorial experiments were further subjected to multi-factor numerical and predictive model to find the optimum condition Bunker C

removal conditions for the two surfactants, and the predicted models were later verified and validated.

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CHAPTER TWO

Determination of Critical Micelle Concentrations of Iveysol® Surfactants with the Tensiometery and Pendant Drop Methods

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CO-AUTHORSHIP STATEMENT

This paper consists of two bodies of work, both of which focused on the determination of the critical micelle concentration (CMC) of surfactants. The first body of the paper, which involved the determination of CMC of the surfactants by Tensiometer method was designed, conducted, analyzed, and interpreted by Abdulrazaq Zubair in the Environmental Laboratory situated at the Faculty of Engineering and Applied Science, Memorial University of Newfoundland (MUN). He had earlier conducted thorough literature reviews on different methods of determining the CMC, and spent considerable amount of time attempting to use the Isothermal Titration Calorimetry (ITC) available in the Biochemistry Department of Memorial University of Newfoundland (MUN), which later proved unsuccessful due to some technical problems with the ITC.

The second segment of the paper was the determination of the CMC of the same surfactants using the pendant drop technique. The experiments were conducted in the laboratory of Dr. Marios Ioannidis at the Chemical Engineering Department, University of Waterloo, Canada. This was done to provide a basis for comparing the results of the two techniques, as literature shows that CMC values vary from one method to another.

Dr. Lesley James and Dr. Kelly Hawboldt reviewed the results, provided technical guidance throughout the experiments, and edited the manuscript.

2.0 INTRODUCTION

Surfactants constitute an important class of industrial chemicals, and are one of the most versatile chemicals [150] widely used in almost every sector of modern industry with an appearance in many diverse products [103, 107]. Their utilization cuts across the petroleum industry [151], chemical and additives manufacturing industries [105], agriculture, pharmaceutical, mining, mineral flotation, paints, soap and detergents, textile, laundry, printing, waste treatments, electronic printing, magnetic recording, biotechnology, research (viral, environmental etc.), woods and food preservative industries etc. [103, 105, 150, 152-154]. During the last decade, the demand for surfactants increased about 300 % within the US chemical industry [155], and the global surfactant market is expected to generate US $41 billion by 2018 [156]. Surfactants are the active ingredients found in soaps and detergents, and are commonly used to separate oily materials from a particular media [42]. In fact, approximately 15 % of the total surfactant production is currently used in oil related applications [157]. This broad utilization and application in different industrial sectors lend credence to their viability as an important chemical product.

Surfactants are surface active agents; a substance that when present at low concentration in a system, alters to a marked degree, surface and interfacial free energies of the surfaces in the system [103]. Structurally, they are described as *amphiphatic* in nature, due to their dual characteristic molecular functional groups,

consisting of a group that has no affinity for aqueous solvents (*hydrophobic group*) and another group that has strong attractions for aqueous solvents (*hydrophilic group*). *The hydrophobic group*s are oil soluble and are always the alkyl hydrocarbon groups of C_nH_{2n+1}-, C_nH_{2n-1}-, C_nH_{2n+1}-, etc., while the *hydrophilic group* which are water soluble include -COO-Na^+, -SO4, -Na^+, -SO3, Na^+, -OH^-, etc. [105]. Surfactants of microbial origin [107], produced from bacteria, yeasts, plants and animals [106] are known as *biosurfactants,* while those produced from chemically based materials. are *chemical or synthetic surfactants* [107]. Depending on the nature of the hydrophilic (head) group, surfactants are classified as *anionic*, *cationic*, *zwitternionic* and *non-ionic* surfactants.

At low concentrations surfactants exist solely as monomers, which accumulate at interfaces present in the system (e.g., air-water, oil-water, soil-water etc.). As the interfacial areas are satisfied and the aqueous surfactant concentration increases, the monomers aggregate to form micelles (as shown in Figure 2.1). The concentration at which the micelles first begin to form is known as the *'Critical Micelle Concentration* (CMC) [108]. It is the solution concentration at which surfactant molecules begin to self-associate to form stable aggregates (micelles) [158]. The term, CMC, was established in the early 1930s by Bury and co-workers [159] in a first reported research into this special characteristic of surface active chemicals.

The CMC is perhaps, the most important property of surfactants, as various physicochemical properties of surfactants and usability in different applications; vary

markedly above and below the CMC value. It is also the simplest way of describing the colloid and surface behavior of a surfactant solute [160]. Moreover, the value determines the industrial usefulness and biological activities of surfactants [161]. CMC also determines a number of interfacial phenomena, such as detergency, solubilization etc., and also affects other interfacial phenomena such as surface or interfacial reduction, that do not directly involve micelles [103]. The CMC is an indicator of the apparent solubility of Hydrophobic Organic Compounds (HOCs), below or the above CMC, in remediation [110]; and a number of enhanced or improved oil recovery processes [104].

The CMC of surfactants can be determined through a number of techniques. The value is typically indicated by a sudden change in a particular physical property of a surfactant solution in response to gradual change or increase in the concentration of the surfactant. The concentration at which this change in property with surfactant concentration happens is regarded as the CMC of such surfactant. The physiochemical properties that can be measured or observed in CMC determination include electrical conductivity, surface tension, light scattering, spectrophotometry etc. Experimentally, a change of slope in a graph of any of the physiochemical properties as a function of surfactant concentration marks the onset of micellization, and hence the CMC value of the surfactant.

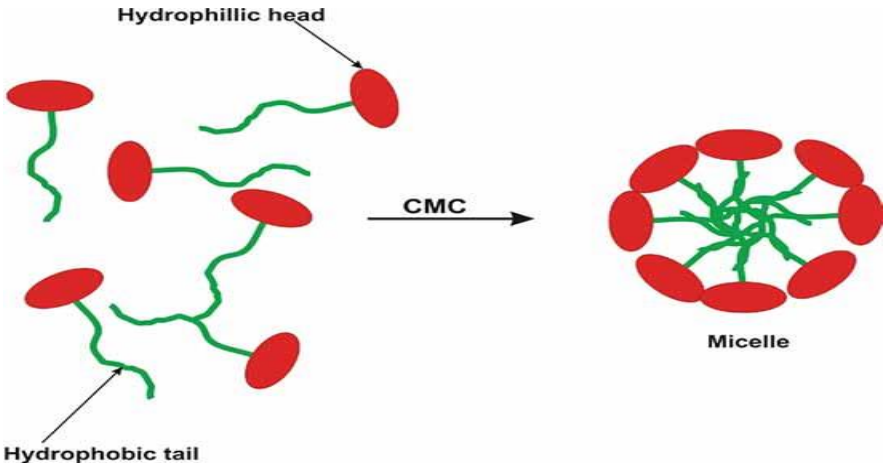


Figure 2.1 Schematic drawing of Micelle Formation
Source: Paul Held [162]

A wide variety of methods have been employed using different analytical techniques and instruments to measure different physiochemical properties of surfactants. This has been made possible by advancement in analytical instrumentation technology in the last decades, with more sensitive and accurate analytical instruments. CMC determination methods which rely on measuring the (electrical) conductivity of (ionic) surfactants with the aid of instruments such as capillary electrophoresis (CE) [163], micellar electrokinetic chromatography (MEKC) [161] etc. have been widely reported. Other methods such as refractive index sensing with fiber sensors [158], heat capacity measurement with isothermal titration calorimetry (ITC) [164], surface tension measurement using a Tensiometer [165, 166] and Pendant drop techniques [154] etc. have also been demonstrated. Other methods such as the use of Nuclear magnetic resonance (NMR) [167], measurement of the speed of sound [168], light scattering

[169], UV absorption spectroscopy [150], fluorescence spectroscopy [150], dye micellization [166] methods etc. have all been shown to be useful in determining the CMC of surfactants.

CMC values are often unambiguous and can differ from one method to another; hence, many studies have attempted to determine the CMC with different techniques or instruments that measure the same physiochemical properties. Domínguez et al [150] investigated the CMC values of three different surfactants using the UV absorption spectroscopy, Fluorescence spectroscopy and electrical conductivity methods. The study found differences in the CMC values obtained from the tested methods. Patist et al [166] also employed the dye micellization and the surface tension methods to determine the CMC of eight different surfactants. There was a 0.97 % to 6.5 % difference between the CMCs measured with these methods. Investigating the CMC using different methods could be based on the premise that several factors can affect the CMC values. These may include nature of surfactant (e.g. ionic vs non-ionic), environmental factors, sensitivity of the analytical instruments among others. Domínguez et al [150] reported that the CMC decreases with increasing hydrocarbon chain-length of the apolar groups in non-ionic surfactants, while the nature and concentration of counter-ions in a solution affect the CMC with the ionic surfactants. Addition of electrolytes; the study further stated, decreases the CMC. Environmental factors such as temperature and pressure are also known to affect the CMC values

[170]. The change in slope that marks the onset of micellization (CMC) occurs over a narrow range of concentrations, whose magnitude depends on the physical property being measured, and on the nature of the data obtained and the way they are plotted [150]. As such, there are interpretation errors associated. Therefore, it is often preferable to determine the CMC through a number of methods.

This study adopted two different methods, namely; the Tensiometer method and the Pendant Drop method, both of which measure surface tension of surfactants to determine their CMC. Three surfactants were studied; the Iveysol® surfactants; namely - Iveysol® 103, Iveysol 106®, Iveysol® 108 – all of which are non-ionic surfactants. The choice of these two methods owes to being widely acclaimed by many authors to providing accurate or near-accurate CMC values. Despite their successful applications for remediation of all kinds of contaminants in the surface and subsurface [51, 52, 76-84], Iveysol® surfactants are not well characterized with respect to their surface-active properties especially, surface tension and CMC. The CMC of Triton X-100, a widely used non-ionic surfactant whose CMC has been reported in many papers [158, 166] was also determined alongside the Iveysol® surfactant formulations.

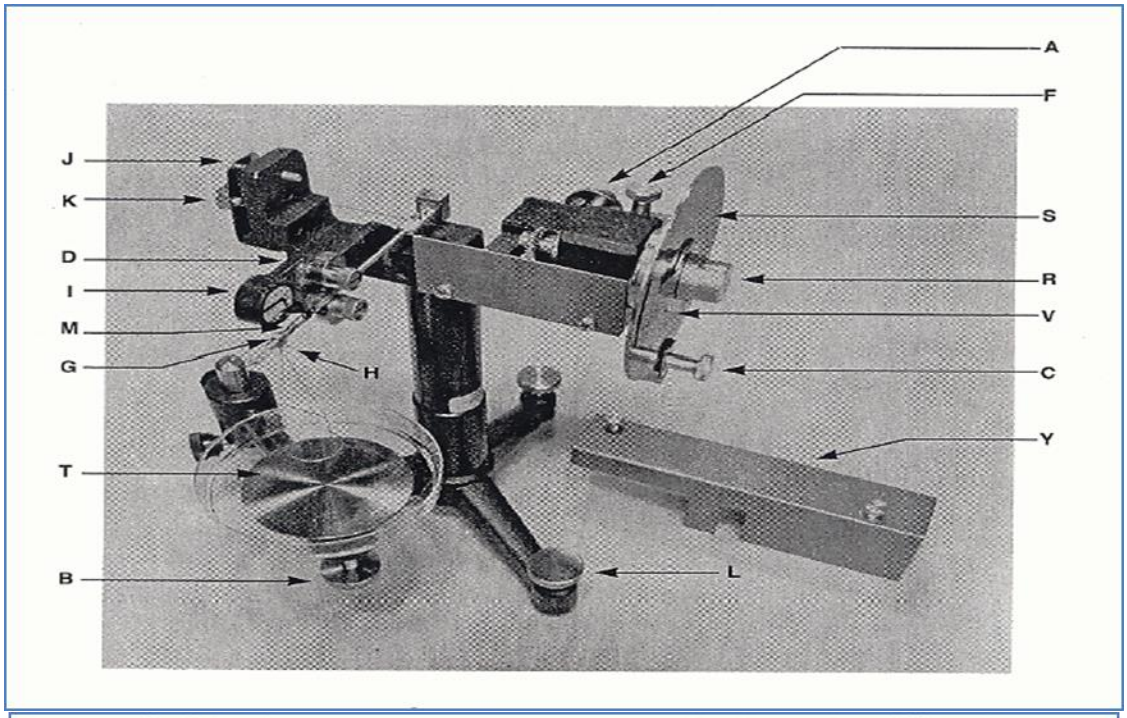
2.1 MATERIALS AND METHODS

The three Iveysol® surfactants used; Iveysol 103®, Iveysol® 106 and Iveysol® 108 formulations were obtained in kind from Ivey International Inc., BC, Canada. The Triton

X-100 was purchased from Sigma Chemical Co., U.S.A. The water used to prepare the surfactant solutions was deionized water produced in an ultrapure water system using UV photo-oxidation at 185 nm (Milli-Q_{185}, Millipore, Bedford, MA). The (CSC Lecomte du Du-Noüy) Tensiometer precision instrument (CSC No. 70535) which conforms to the specification of ASTM Standard Method D971-50 was used for the tensiometer method, while the pendant drop method was accomplished using the laser tensiometer LASDA Mk IV (D. and R. Ferstl GmbH, Hemau, Germany).

2.1.1 The Tensiometer Method

The determination of surface tension of pure liquids and their solutions using the CSC Lecomte du Noüy ring tensiometer is a frequently used method for the determination of surface tensions of surfactant solutions [171]. It is an absolute method which determines the surface tension without reference to any other method [171] while taking into account well known precautions and reproducible results within an error range of ± 0.1 mN/m for solutions of non-ionic, anionic and amphoteric surfactants [172]. The method allows for measurements to be made within 15 to 30 seconds on each sample and is regarded as the only method that gives satisfactory results for colloidal suspensions which exhibit rapid changes in surface tension within a very short time [165]. Other advantages in addition to speed of measurement, as highlighted by previous researchers include the elimination of mathematical calculations, and reduction in the quantity of test liquid required [173].



A	Knurled Knob	L	Base Leveling Screw
B	Sample Table Adjustment Screw	M	Torsion Arm
C	Dial Clamp	N	Knurled Release
D	Adjustable Stops	P	Vertical Arm
E	Counter Weight	R	Cap
F	Fine Adjustment Screw	S	Dial
G	Adjustment Nuts	T	Sample Table
I	Index	V	Vernier
J	Wire Retaining Screw	X	Clamping Jaws
K	Rear Clamp Spring Support	Y	Torsion Wire Cover

Figure 2.2: The CSC Lecomte du Du-Noüy Tensiometer

Source: CSC Du-Noüy Tensiometer Manual [174]

The surfactants were diluted with deionized water into different concentrations. About 40 ml of each of the surfactants to be measured was placed in a 65 ml sampling jar (bottle). The container was placed on the sample table. The ring was raised to the uppermost position until the platinum ring was submersed approximately 5 mm in the

surfactant by using the sample table adjustment screw (B). The assembly was lowered until the platinum ring was just below the surface of the surfactant and the platinum ring was centered in the container. The platinum ring was then lowered further by using the sample table adjustment screw (B), until the platinum ring was just on the surface and the index (I) was approximately at zero. The torsion of the wire was increased using the knurled knob (A) and simultaneously lowering the sample table with adjustment screw (B) to keep the index (I) at zero until the surface film breaks, as shown in Figure 2. The reading on the scale when the film breaks, is recorded as the surface tension. The above methodology is repeated for other surfactant formulations. All experiments were replicated three times, and were conducted at an ambient temperature of 22 ^{o}C.

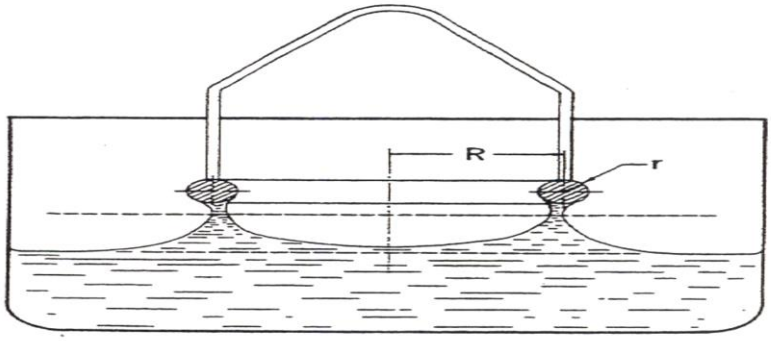


Figure 2.3 Condition of the Surface Film at Breaking Point
Source: CSC Tensiometer manual [174]

2.1.2 The Pendant Drop Method

The pendant drop tensiometry technique is considered to provide very accurate surface tension measurements [154]. In measuring the surface tension, the surfactants were made into different concentrations and the surface tension measurements were

performed with a Laser Scanning Drop Shape Analysis (LASDA) tensiometer, following the measurement principle fully described by Semmler and Kohler in their studies [154, 175]. The auto-calibrated tensiometer was operated from a PC equipped with software for automatic measurement and simultaneous calculation of the interfacial tension using Laplace's equation. The dynamic interfacial tension is continuously shown on the monitor. The information obtained from the laser scanner is used to control drop volume, drop formation, and breakoff as well as drop vibrations. Each surface tension isotherm consists of 14 to 22 single points (surfactant concentrations). Each point is a mean value of three to five different drops. A capillary made of high quality stainless steel of gauge 12 was used. Drop volumes were in the range of 19 – 32 ml, depending on surface tension and surfactant concentration. Temperature was kept constant at 25 °C and the final value of the surface tension was measured after 63 minutes. The experiment was repeated three times for each surfactant.

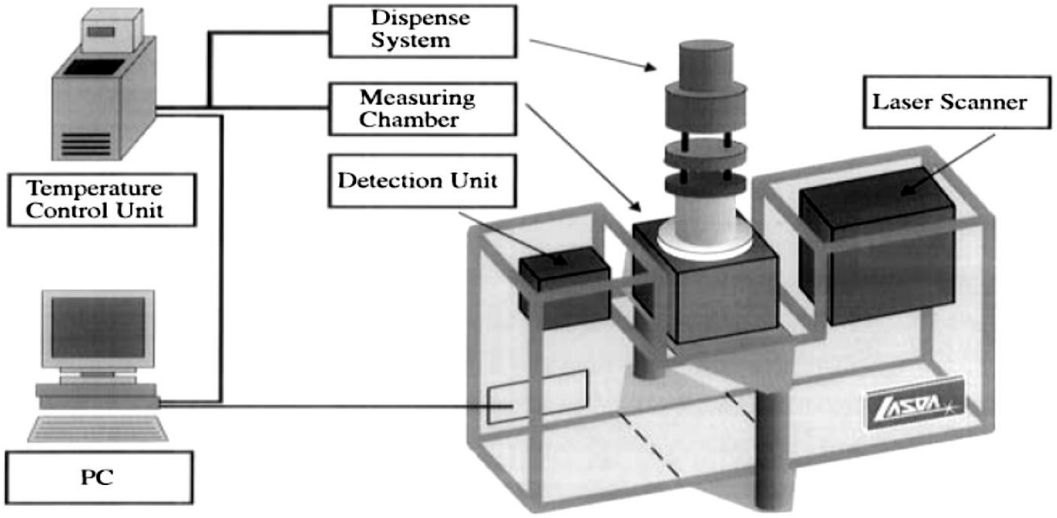


Figure 2.4 Essential Components of Laser Scanning Drop Shape Analysis System
Source: Semmler

2.2 RESULT AND DISCUSSIONS

Table 4.1 summarizes the average CMC values obtained from the Pendant Drop and Tensiometer methods. Although both methods measures the same physiochemical property (surface tension), the CMC values obtained from Tensiometer method are approximately 1.1 to 4.1 times higher than those obtained from the Pendant drop technique. Theoretically, the two methods rely on the principle that surface tension of surfactants reduces with increased concentrations, and remains constant once the CMC is reached. The surfactant concentration where the surface tension remains constant marks the onset of micellization, and such concentration is the CMC of such surfactant.

The graphical illustration of the analyses of the data and subsequent determination of the CMC values are shown in Figures 2.5, 2.6 and 2.7.

Table 2.1 CMC as Determined by Tensiometer and Pendant Drop Methods

Surfactant	Pendant Drop Method	Tensiometer Method	$\frac{\text{CMC Tensiometer}}{\text{CMC Pendant Drop}}$
Iveysol® 106	0.029 %v/v	0.025 %v/v	0.9
Iveysol® 108	0.020 %v/v	0.025 %v/v	2.5
Triton X-100	133.5 %v/v	135.5 %v/v	1.0

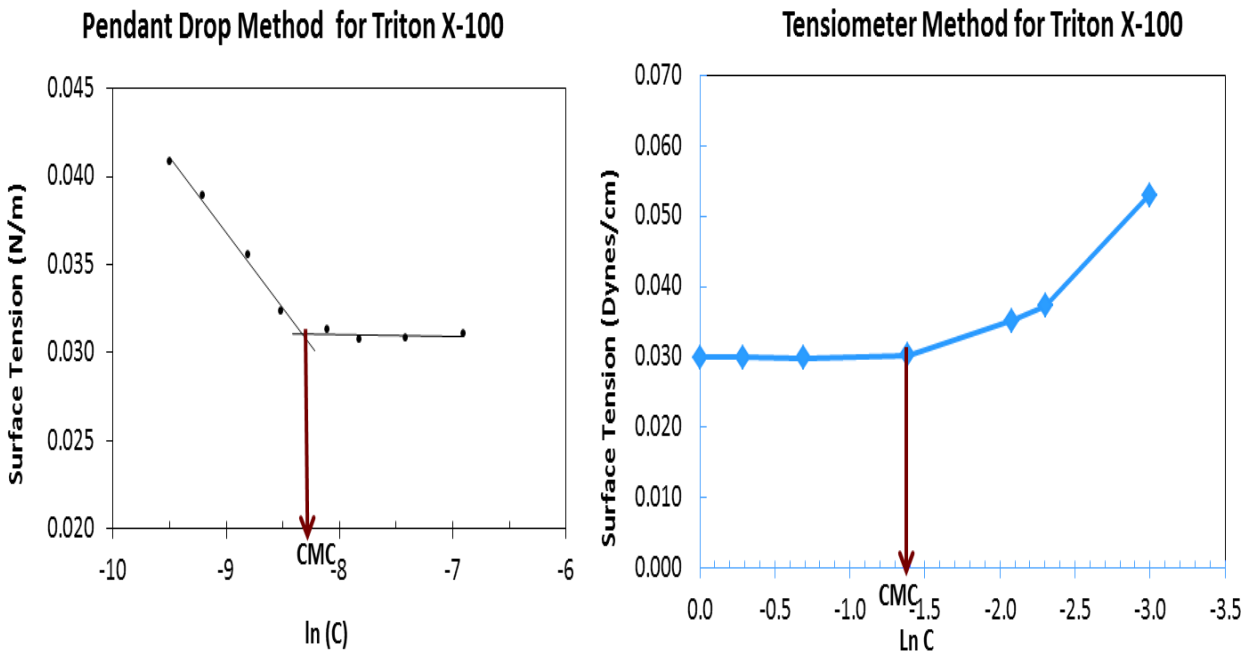


Figure 2.5 CMC Determination for Triton X-100

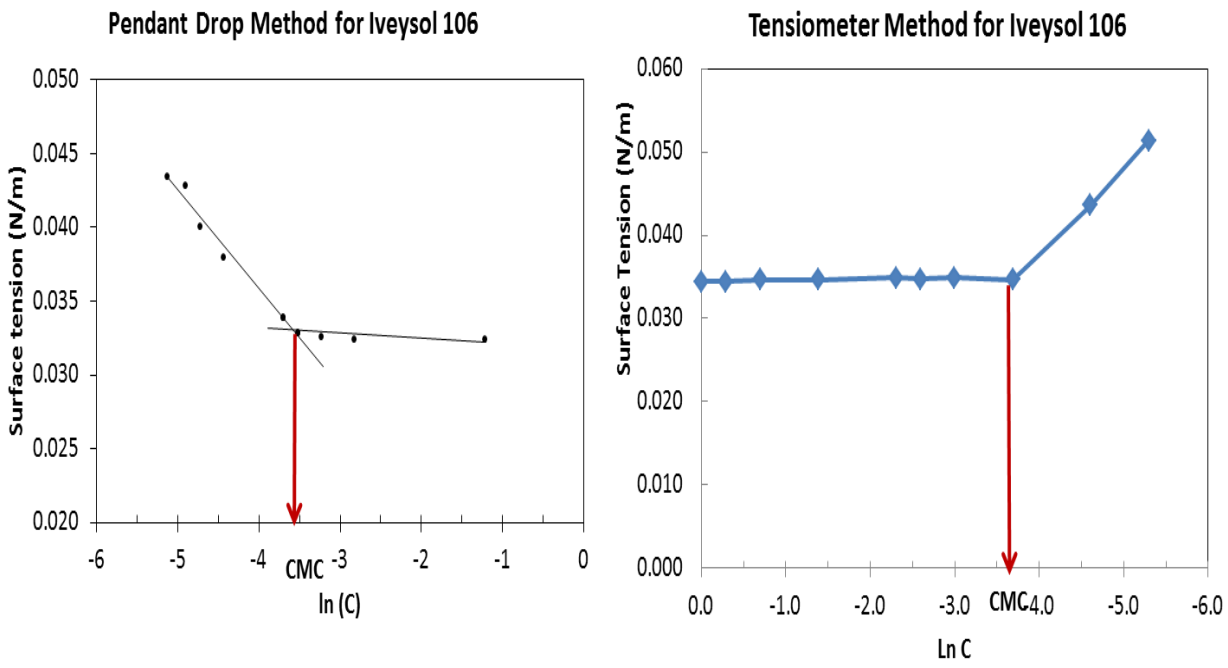


Figure 2.6 CMC Determination for Triton Iveysol® 106

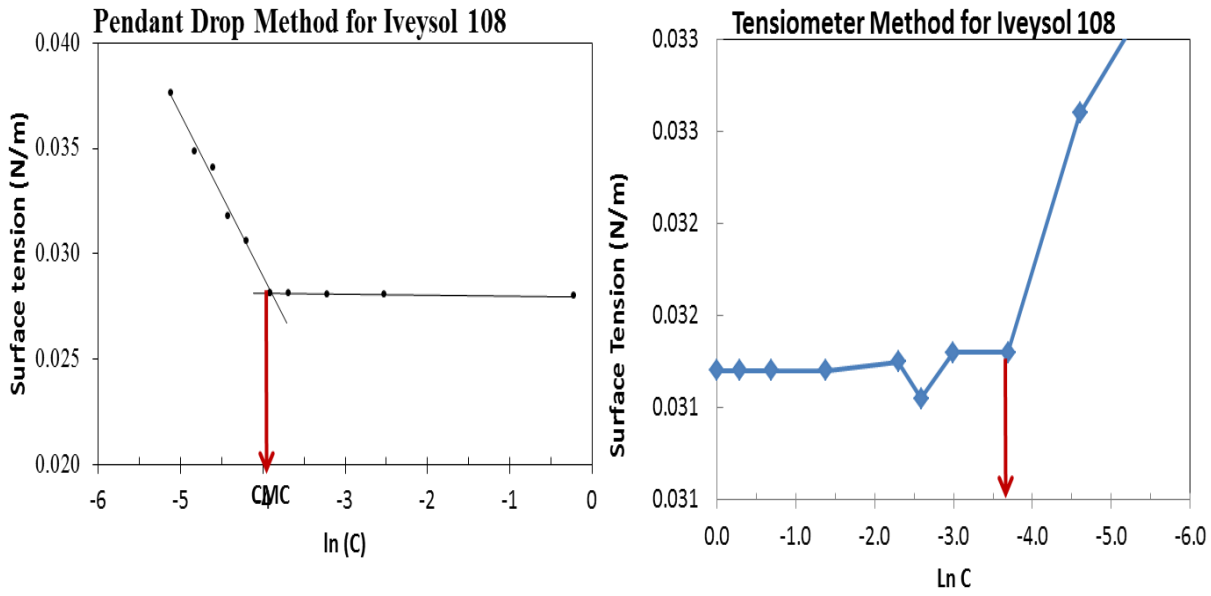


Figure 2.7 CMC Determination for Triton Iveysol® 108

The CMC values obtained from both methods for Triton X-100, i.e. 133.5 %v/v (022 mM) and 135.5 %v/v (0.24 mM) fall within the range obtained by several previous researches. Patist et al [166] recorded a CMC of 0.20 mM through dye micellization method, while Tan et al., [158] reprted a CMC of 0.21 mM in their study in which they used fibre-optic refractive index to determine the CMC of Triton X-100. The Sigma Aldrich's [176] Material Safety Data Sheet (MSDS) and product information also report a CMC range of 0.22 – 0.24 mM for Triton X-100. There is no published data with which to compare the CMC of Iveysol® surfactants.

The marginal differences in the CMC values from both methods are not unexpected due to the differences in methods. Patist et al., [166] compared the measurement of CMC of surfactants with dye micellization and surface tension methods recorded CMC values that were approximately 1.6 to 6.5 times different in values. Inuoe [169] studied the micelle formation of surfactants by NMR and light scattering methods, the results of which showed different CMC values. In this study, Iveysol® 106 and Triton X-100 gave CMC values that were very close to each other, this was probably due to the fact that these samples do not contain large amount of impurities or a wide distribution of ethoxylation and those like Iveysol® 103 and 108 that gave wide different CMC values are suspected to contain impurities [166]. An impure surfactant, will have a higher absorption coefficient [177, 178], which can saturate the surface and exhibit constant surface tension without any micelle formation in the bulk solution [166], thereby giving

a wrong CMC value. Foam fractionation can purify the surfactants. It is a surfactant purification method which basically require adsorption of solute species at gas-liquid interface between a dispersed phase (gas bubble) and a continuous phase (bulk liquid) [166].

2.3 SUMMARY AND CONCLUSIONS

This is the first study to look into the CMC of Ivesyol surfactants, even though these surfactants have been used in different industrial applications for the remediation of various hydrocarbon contaminants, at different high-profile brownfield sites. The study understood the importance of finding the CMC values of these surfactants, especially as the overall objective is to use them for Bunker C fuel oil remediation at concentrations below their CMC values.

Various studies have underscored the importance of determining CMC values with different methods owing to the unambiguous nature of the CMC value, especially, as it depends on several factors, notable among which is temperature and purity of the surfactants. In this research, two widely acknowledged reliable methods have been used to determine the CMC of Iveysol® surfactants. Although the CMC values from both methods vary as expected, the variation can be attributed to the effect of temperature on surface tension measurement [150, 154, 166]. The experiments were both

conducted under ambient temperatures, the possibility of slight variations in the room temperatures cannot ruled out, and may have affected to some extent, the CMC values. Purity of the surfactants is another important factor which may have contributed to the differences in the CMC values. The Iveysol® surfactants were received in diluted solutions, therefore, it can be assumed that there might be some impurities in the surfactants. This study will recommend further investigations to determine the CMC with purer forms of the surfactants.

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CHAPTER THREE

Development, Optimization, Validation and Application of a GC-FID Method for the Analysis of Total Petroleum Hydrocarbons (TPH) in Contaminated Soils

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ABSTRACT

The reference method for the Canada-Wide Standard (CWS) for Petroleum Hydrocarbon in soil is used for the analysis of petroleum hydrocarbon compounds across Canada. However, inter-laboratory application of this method for the analysis of Total Petroleum Hydrocarbon (TPH) in the soil has often shown considerable variability in the results. This could be due, in part, to the different gas chromatography (GC) conditions, soil properties, as well as and other steps involved in the method. In addition, there are differences in the interpretation of the GC results, which impacts the determination of the effectiveness of remediation at hydrocarbon-contaminated sites. In this work, multivariate experimental design approach is used to develop and validate the analytical method for the quantitative analysis of TPH in (contaminated) soil. A fractional factorial design (fFD) was used to screen six factors to identify the most significant factors impacting the analysis. The most important factors were then optimized using a central composite response surface design. Robustness testing and validation of model compares favourably with the experimental results with percentage difference of 2.78 % for the analysis time. The method was successfully applied for fast analysis of TPH of Bunker C oil in contaminated soil.

CO-AUTHORSHIP STATEMENT

The principal author is Abdulrazaq Zubair, who in the course of utilizing the GC-FID for Bunker C oil analysis identified some lapses in the existing CCME Canada Wide Standard method, performed all the literature searches required for the background information, conducted the experiments and wrote the paper. The co-authors are Dr. Lesley A. James, and Dr. Kelly Hawboldt, who provided technical guidance and edits in their capacities as supervisors, while Dr. Michael Pappoe; the second author, assisted with experimental design and identification of the analytical parameters.

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3.0 INTRODUCTION

In the past, there was no standard method for the analysis of total petroleum hydrocarbon (TPH) in the soil in Canada, leading to differing analytical methods and regulations in different jurisdictions. Methods used for the analysis of TPH in the soils typically varied across commercial laboratories. This did not only make it difficult to compare analytical results, but also caused over- or under-estimation of contaminated sites under remediation, as well as affected the effectiveness of remediation services and technologies. The need to develop a harmonized methodology for analysis of petroleum hydrocarbon compounds (across Canada) became necessary to remove these uncertainties. Turle *et al.,* (2007) [179] reviewed the Canadian Council of Ministers of Environment (CCME)'s Analytical Method Technical Advisory Group's (AMTAG) process in developing the reference method for the Canada-Wide Standard (CWS) for Petroleum Hydrocarbons (PHC) in Soil – Tier 1 Method (CCME-CWS method) [180]. This methodology is designed for the assessment and remediation of contaminated sites, and requires that four petroleum fractions be determined analytically by a combination of extraction and Gas Chromatography (GC). The fractions are based on molecular weight. The first fraction, F1, includes hexane to decane (C_6 - C_{10}); the second fraction, F2, includes decane to Cyclohexane (C_{10} - C_{16}). The third fraction, F3, includes Cyclohexane to Tetratriacontane (C_{16} - C_{34}), and the fourth fraction, F4, from Tetratriacontane to Pentcontane (C_{34} - C_{50}) respectively. Gravimetric heavy hydrocarbon

(F4G) is defined as the extremely heavy carbon fraction (above C_{50}) and determined (by gravimetric and not chromatographic analysis) only if the chromatogram of the F4 (C_{34} to C_{50}) hydrocarbon fractions fail to return to baseline at or above C_{50}.

The limitations in the published method became apparent in our research related to a project [84] on analyzing the effectiveness and developing a protocol on soil remediation using surfactants. In the course of analyzing soils contaminated with Bunker C oil using the CCME method, and following the sample preparation procedures stated in the published method, most of the carbon fractions were not eluting in the chromatogram. The sampling period of 20 minutes specified in the method was also perceived to be too long. The researchers had an inkling that this variability in the chromatographic output in which most of the carbon fractions were not eluting may be due to the GC chromatographic conditions as well as use of inappropriate solvents. Although other factors such as errors during sample preparation and extraction, interferences from natural organic content of the soil, and from soil amendment procedures [2] can also lead to variability in hydrocarbon analysis in the soil. Other studies in the past have also reported disparities in published analytical methods. Saari *et., al.* [181] did an inter-laboratory comparison of TPH analysis using the International Organization for Standardization (ISO) and European Committee for Standardization (CEN) standards, and reported wide discrepancies in methodology and results. Similar

studies attributed these kind of differences (in analytical methods) to GC calibration [182, 183]. Therefore, these discrepancies are not unexpected [181].

The gas chromatography (GC) is perhaps one of the most robust analytical instruments for analyzing volatile compounds such as TPH. The ability to couple highly sensitive detectors such as the flame ionization detector (FID) and mass spectrometry (MS) makes it a choice for highly sensitive petroleum analysis. The FID detects ions produced during the combustion of compounds (separated by gas chromatography) in a H_2/air flame. The FID response depends on the number of ions produced by a compound. Since this varies considerably between compound classes, FID response factors vary correspondingly [184, 185]. The ability of a chromatographic method to successfully separate, identify and quantify species is determined by many factors [186]. The identification of these significant operating factors can be facilitated by multivariate statistical methods and result in better overall methodologies.

Multivariate experimental designs are a statistical methodology which allows for systematic variation of multiple factors within one experimental design, and the use of the results to create mathematical models for the experiments. Using these models, the optimum conditions (factors) of a process are determined, interactions between, and the most important factors into that process are revealed [187]. This statistical approach is particularly useful in quantitative analysis when several experimental factors have to be optimized. It is especially more important in regulatory or forensic research such as

pharmaceutical active ingredient screening, environmental contaminant analysis, and criminal investigations, as these methods require not only fast analysis but also reliable analytical results. They also ensure the efficient use of time and resources provide information about the physio-chemical properties of the system, and allow for prediction of responses based on experimentation. In addition, there are robust and reliable statistical tools (software) to aid in the design and model fitting [186]. The most commonly used multivariate designs are the fractional factorial and full factorial designs, and the more complex response surface designs such as the Central Composite, Box-Behnken, Doehlert and mixture designs.

A large number of applications of multivariate approaches for optimization of different chromatographic analytical methods have been reported in the literature, in applications such as High Performance Liquid Chromatography (HPLC) [1, 2], GC - Mass Spectrometry (GC-MS) [3, 4], GC-FID [188, 189], Capillary Electrophoresis - UV detection (CE-UV) [190], and Micellar Electro-kinetic Chromatography (MEKC) [191, 192].

The objective of this study was to use multivariate experimental design approach to modify, optimize and validate an improved and faster CCME Canada Wide Standard method for TPH analysis in the soil, for a more reliable total petroleum hydrocarbon analysis. The specific objective was to determine the optimum GC operational settings and conditions for a more reliable and faster TPH analysis with this method.

The work is divided into four sequential phases. The first phase (section 3.2.1) involved the screening experiments, designed to identify the experimental factors that were most important, and which factors do not significantly affect the experimental results. Fractional factorial (fFD) design was used to screen six (6) factors, namely - injection volume (µL), injection temperature (°C), oven program ramp up (°C/min), detector temperature (°C), carrier gas flow rate (mL/min) and solvent ratio (v/v hexane/dichloromethane). In the second phase (section 3.2.2), optimization experiments were conducted in which the significant factors identified from the screening experiments were optimized using a Central Composite Response Surface Design (CCD). In the third phase (section 3.2.3), optimized conditions were tested for robustness and the developed model was validated by calibrating the GC system with a hydrocarbon standard using the optimized GC settings. The fourth and final phase (section 3.2.4) involved application of the optimized experimental conditions for the analysis of real hydrocarbon (Bunker C oil) sample.

3.1 MATERIALS AND METHODS

3.1.1 Chemicals

The hydrocarbon standard used for calibration was a Supelco 1000 µg/mL of hydrocarbon mix in Cyclohexane (Sigma-Aldrich, Canada) and contained a mixture of decane (C_{10}), hexadecane (C_{16}), tetracontane (C_{34}) and pentacontane (C_{50}) in cyclohexane (F2 to F4 fractions). Other reagents used included hexane, acetone, and

methanol (Fisher Scientific, Canada), dichloromethane (ACP Chemical Company, Canada), anhydrous sodium sulfate, and the silica gel (Sigma-Aldrich, Canada). All the solvents were ACS reagents/certified.

The Bunker C oil sample used to test the method was extracted from a soil contaminated with Bunker C fuel oil. The soxhlet extraction method was used following the procedure outlined in the CCME reference method [180].

3.1.2 GC-FID Instrumentation

The TPH analyses were performed on an Agilent Technology gas chromatography system 7890A, equipped with an Auto Sampler 7693 (Agilent Technology), and an FID. Data were acquired and processed using Agilent OpenLAB Chromatography Data System (CDS) Chemstation Edition for integrated peak areas, peak heights, and elution and analysis times. The GC used a MXT®-1 Columns (nonpolar phase; Crossbond® dimethyl polysiloxane) with a maximum temperature capacity of 430^{o}C, 15m x 250 µm x 0.1µm dimension (RESTEK Chromatographic Solutions, Canada). Splitless injection was used for all the experiments. The carrier gas used was helium, the make-up gas was nitrogen, and hydrogen was used as the fuel gas.

3.2 RESULTS AND DISCUSSIONS

3.2.1 Screening Experiments

3.2.1.1 Experimental Design

Minitab® 17.1 was used for the design and analysis of the experiments. A 2^{6-2} fractional factorial design was used for screening the six quantitative factors (solvent mixture, oven programming, injection volume, injection temperature, carrier gas flow rate, and detector temperature) to identify the most critical factors for optimization. A resolution IV with one centre point was used where the main effects of the varied factors are cofounded in a 3-way interaction. This approach allows for better estimation of the effects of the experimental factors on the response(s) and therefore, better selection of the significant factors for optimization [193]. The screening design required a total of 17 experiments. The factors investigated and their levels are presented in Table 3.1.

The solvent mixture is the mixture ratios (v/v) of hexane and dichloromethane in which the hydrocarbon standard mixture was prepared prior to injection. For the oven programming, the initial set temperature was 50 ^{o}C for 0 minutes and the temperature ramping (rate) was varied according to the table to a final temperature of 350 ^{o}C and held for 5 minutes. All injections were done in the splitless mode.

Table 3.1 Factors and their Levels Used in the Screening Experiments

Factor	Unit	-1	0	+1
Solvent mixture	v/v	50/50	70/30	90/10
Oven Programming (Ramp 1)	^{o}C	25.0	37.5	50
Injection Volume	µL	1.0	2.0	3.0
Injection Temperature	^{o}C	300	350	400
Carrier Gas (Helium) flow rate	mL/min	1.5	2.75	4.0
Detector Temperature	^{o}C	300	350	400

The responses studied for these set of experiments were the peak resolution factors (R) for adjacent peaks, height of peaks (H), and the analysis time (t) in minutes. The R was calculated using the following equation:

$$R_{1-2} = \frac{2\,(t_2 - t_1)}{w_1 + w_2} \qquad (1)$$

where t_2 and t_1 are the migration times of two adjacent peaks and w_1 and w_2 are the baseline peak widths. See Table 2 for further description of the responses selected for these (screening) experiments.

Table 3.2 Responses Selected for the Screening Experiments

Response	Description
R_{1-2}	Resolution for peaks of C_{10} – C_{16} (F2)
R_{2-3}	Resolution for peaks of C_{16} – C_{34} (F3)
R_{3-4}	Resolution for peaks of C_{34} – C_{50} (F4)
H_1	Height of C_{10}
H_2	Height of C_{16}
H_3	Height of C_{34}
H_4	Height of C_{50}
t	Analysis time

3.2.1.2 Results and Discussion of Screening Experiments

The effects of the critical factors on the selected responses were statistically analyzed using the Pareto chart of effects tool. The Pareto chart is an important statistical tool useful for visual identification of significant and less significant factors in a set of multivariate experiments. It uses the t-value of the absolute effects and scales experimental effects in terms of standard deviations [88]. Any experimental factor(s) that extends beyond the t-limit value (the vertical dash-lines) is considered a significant parameter at 95% confidence level. Studies such as Pandey *et al.,* [194], Puertas *et al.,* [195] etc. made use of pareto charts. The Pareto charts showing the significance of the

screening factors for peak resolution, peak heights and the analysis time responses are presented in Figures 3.1, 3.2, and 3.3 respectively.

The different responses selected were used to evaluate the analytical performance of the factor combinations, however, the adjacent peak resolution factors and analysis time were selected for optimization as they are critical for method development and validation. Based on these two responses, the carrier gas flow rate and oven programming were the most critical factors, as they were the factors that significantly affected peak resolution and analysis time based as shown in the pareto charts. This selection was also based on the premise that in the screening experiments, all the four compounds (fractions) successfully eluted with complete (high) resolutions at a maximum analyses time of 13.3 minutes and within the shortest (minimum) time of 8.8 minutes. Therefore, eliminating the need to further evaluate the effects of the factors on the height of the peaks in the subsequent optimization experiments. In most commercial laboratories, it takes nearly 20 minutes before the C_{50} (F4) elutes. Therefore, the optimization experiments were designed with a shorter analysis time in mind as well as visible, high-resolution peaks for all the compounds (fractions) of interest.

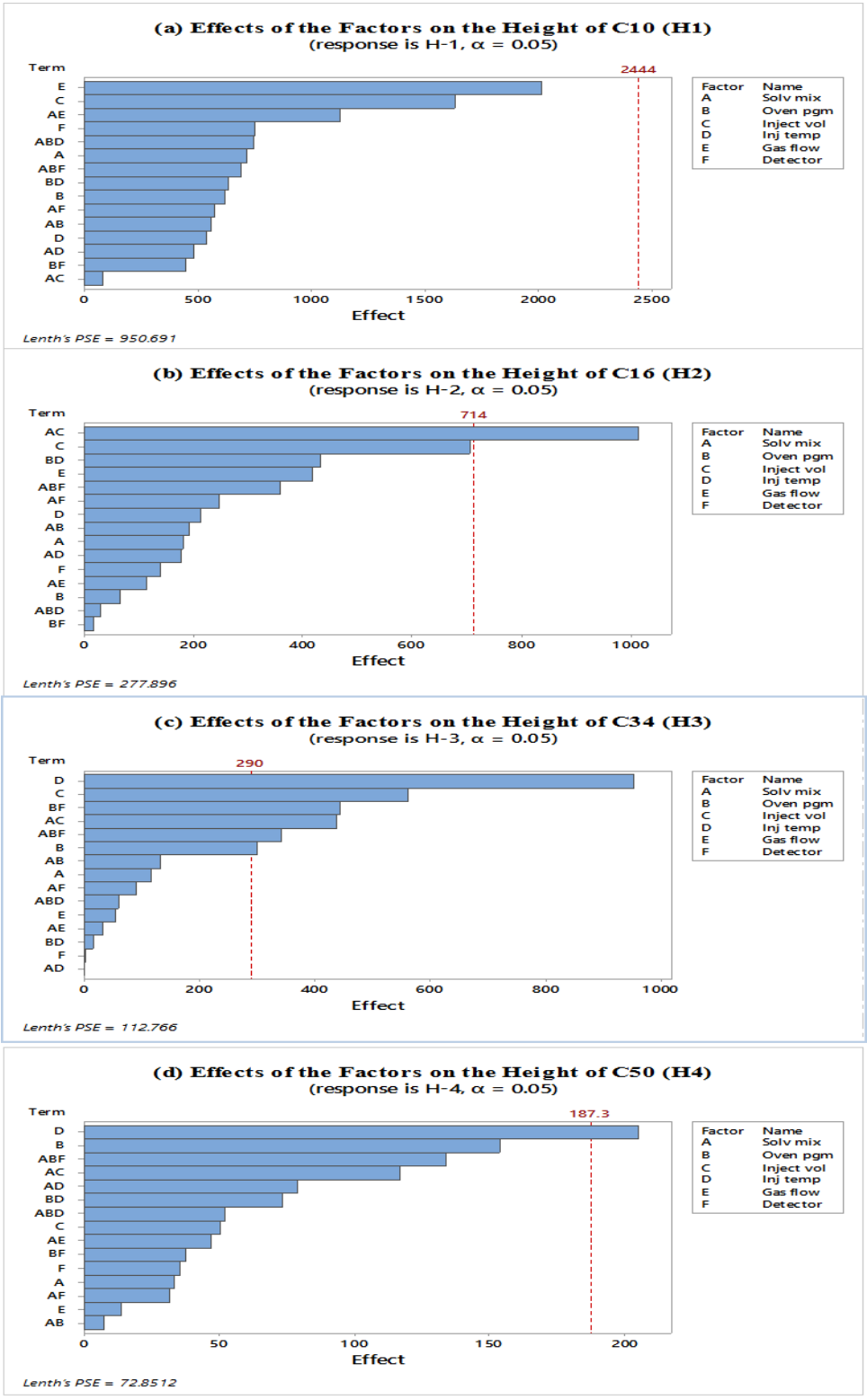

Figure 3.1 Pareto Charts for Effects of the Factors on Peaks Height

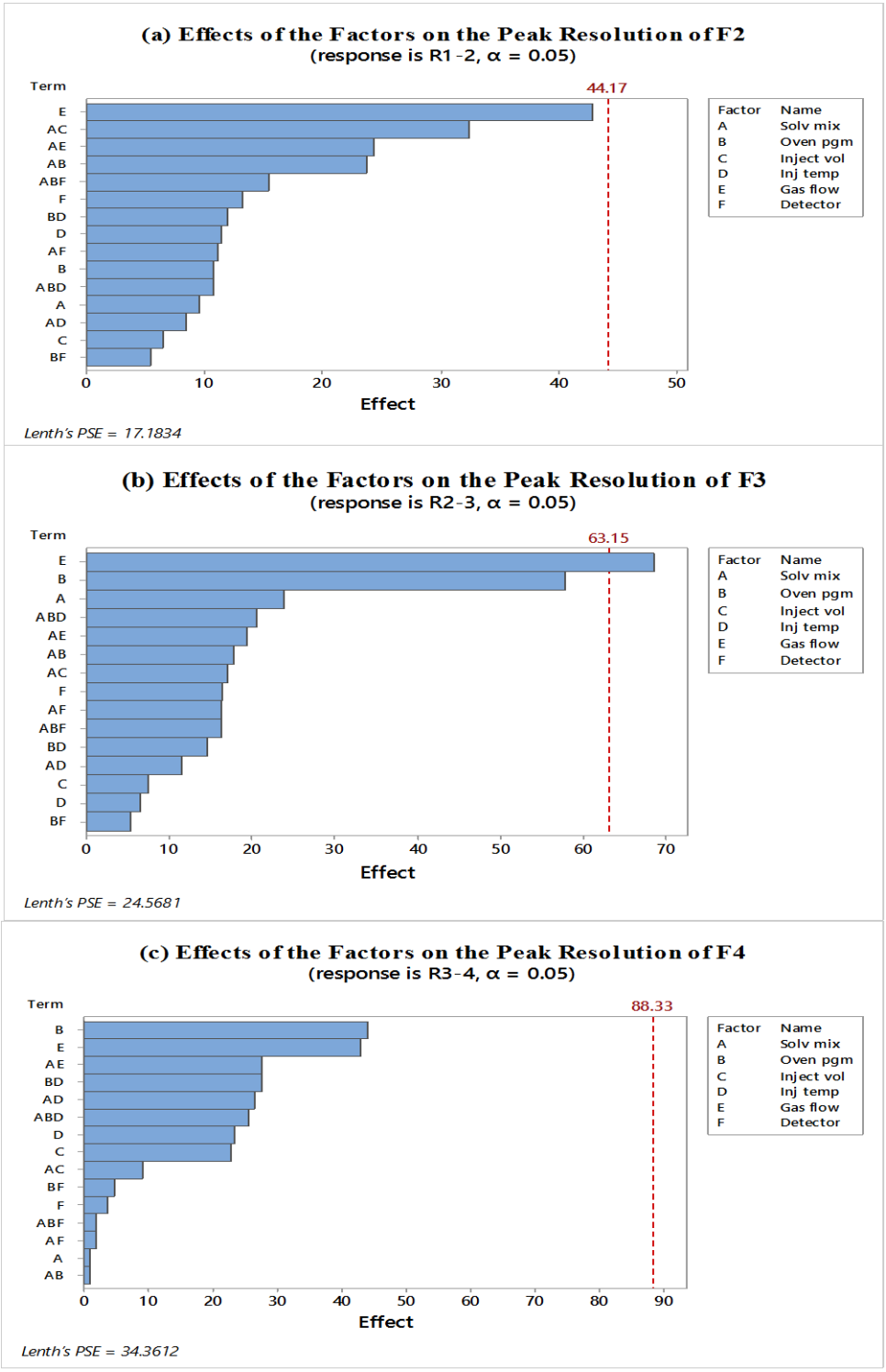

Figure 3.2 Pareto Chart for Effects of Factors on Peak Resolutions

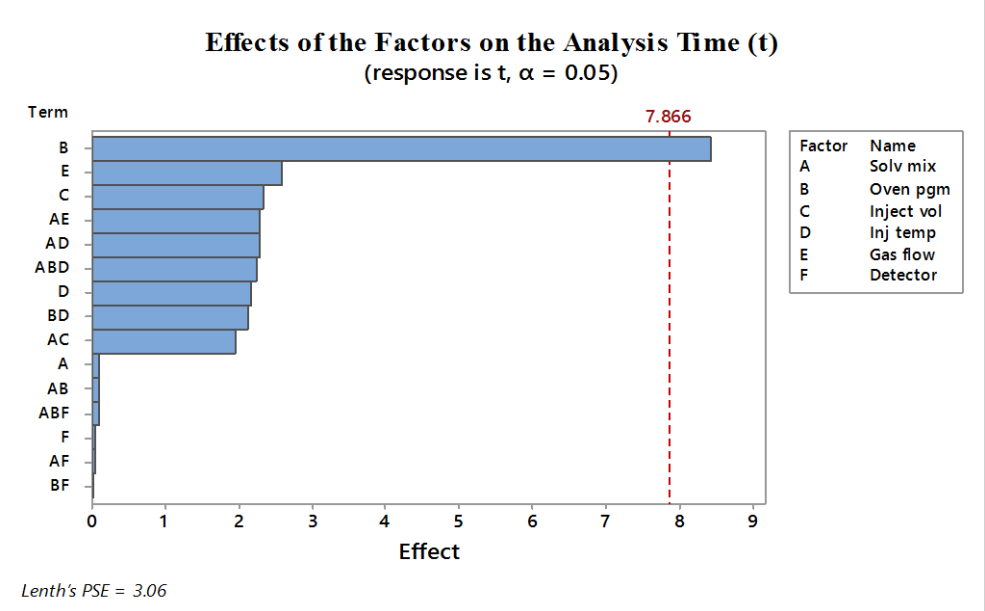

Figure 3.3 Pareto Chart for Effects of Factors on Analysis Time (t)

3.2.2 Optimization Experiments

3.2.2.1 Design of Optimization Experiments

A central composite design (CCD) response surface methodology was employed in designing the optimization experiments. CCD is used to determine the optimum operation conditions after the significant factors have been identified [196]. It allows greater number of analyses to be conducted without performing experiments at every combination of factors levels. It also combines a two-level factorial design with a star design and centre points [186]. The optimum factor settings for the desired responses are expected to be in the experimental domain of the response surface. The optimized factors (gas flow and oven program) were varied, while the other factors were fixed at

the maximum levels which they were used in the screening experiments. Table 3.3 shows the experimental levels for the factors used in the optimization experiments (designed with Minitab® program) and generated a total of thirteen (13) experimental runs, with the peak resolution factors (R_s) for adjacent peaks and the analysis time (t) as the studied responses.

Table 3.3 Central Composite Design (CCD) Optimization Experiments

Factor	Unit	-1	+1
Factors optimized			
Oven Programming (Ramp 1)	^oC/min	25	50
Carrier Gas (Helium) flow rate	mL/min	2.0	5.0
Factors fixed			
Solvent mixture (hexane/dichloromethane)	v/v	90/10	
Injection Volume	µL	3.0	
Injection Temperature	^oC	400	
Detector Temperature	^oC	400	

The results of the optimization (Table 3.4) show a complete elution of all the compounds with well-defined peak resolutions and the lowest analysis time of 8.26 minutes. Based on these results, the response surface design fits a quadratic model to predict the response as a curved function of the factors selected. Since separation in GC is based on retention of the analytes on the stationary phase, the analysis time is a good

marker for predicting the behaviour of the analytes. Thus, we generated an equation for the regression model based on the factors selected for the optimization experiments calculated for the analysis time (t), which is given below (in un-coded units):

$$\mathbf{t = 28.52 - 0.236}x \mathbf{- 0.7846}y \mathbf{+ 0.0069}x^2 \mathbf{+ 0.007748}y^2 \mathbf{- 0.00040}xy \quad (2)$$

where x is the gas flow (mL/min) and y is the oven program (°C/min). With this regression model, the retention behaviour can be predicted by iteration to obtain the desirable response. As an alternative, a response optimizer (Minitab® feature) can also be used to predict response based on a given criteria.

The targets set for optimizing the responses are shown in Table 3.5. Minitab uses a desirability function to calculate an individual desirability (d) for each of the responses and weights assigned to it. The overall (composite) desirability (D) is then determined from the combined desirabilities. The composite desirability function used in constructing the optimization parameters utlizes the weighted average of the geometric means of the individual desirability of the factors in achieving the targeted settings. It assesses how well a combination of variables satisfies the goals defined for the responses and evaluates how the settings optimize a set of responses overall. Desirability has a range of zero to one. Assigning a value of one to a factor represents the ideal case; while zero indicates that one or more responses are outside their acceptable limits.

Table 3.4 Layout and Results of Optimization Experiment

Pt Type	Gas flow (mL/min)	Oven program (°C/min)	R_{1-2}	R_{2-3}	R_{3-4}	t (min)
0	3.50	37.50	135.00	154.00	73.00	9.20
-1	1.38	37.50	136.20	190.38	102.19	9.76
0	3.50	37.50	135.20	152.39	74.56	9.16
1	2.00	25.00	124.10	181.85	95.63	13.01
-1	3.50	55.18	316.10	134.66	73.29	7.83
1	2.00	50.00	93.18	138.96	86.54	8.26
0	3.50	37.50	148.70	155.41	72.17	9.14
-1	5.62	37.50	420.60	162.21	63.79	8.87
1	5.00	50.00	240.20	123.57	66.29	7.66
0	3.50	37.50	146.60	157.01	76.47	9.39
-1	3.50	19.82	125.8	168.71	80.61	15.58
0	3.50	37.50	147.70	157.98	75.09	9.11
1	5.00	25.00	140.30	174.89	71.44	12.44

Table 3.5 Model Optimization Parameters

Response	Goal	Lower	Target	Upper	Weight	Importance
Time (t)	Minimum	8	10	10	10.0	10.0
R3-4	Target	45	50	150	0.1	0.1
R2-3	Target	45	50	150	0.1	0.1
R1-2	Target	45	50	150	0.1	0.1

Since the peaks were well resolved in each of the previous experimental phases (at both screening and optimization stages), the desirability of the analysis time (t) was assigned a higher importance (10.0) than the resolution (R) responses (0.1). Also, Minitab's® Response Optimizer allows for the calculation individual factor desirability by assigning a weight (from 0.1 to 10) to determine how much to emphasize in obtaining the target value. Based on the aforementioned reason, a weight of 10.0 was assigned to analysis time (t) and 0.1 to peak resolutions (Rs) as shown in Table 3.5.

The model's goodness of fit is shown in Table 3.6. The higher percentage differences for $R_{1\text{-}2}$ (peak resolution for F2, i.e. $C_{10} – C_{16}$) and $R_{3\text{-}4}$ (peak resolution for F3, i.e. $C_{16} – C_{34}$) are due to the skew in weighted averages to the analysis time as explained previously. However, there was a good fit of the model in the response prediction.

3.2.3 Validation of Optimum Experimental Conditions for TPH

The optimum conditions given by the model shown in Table 3.6, were used to analyse an analytical standard mixture containing all the hydrocarbon fractions (F1 to F4) in the validation experiments, the analysis was replicated three times (n = 3), and the mean of the analyses was recorded as the analysis time (t). An example of the chromatograms obtained from the analyses is shown in Figure 3.5. The predicted responses (model) of the analysis time (t) were compared with the experimental values and are tabulated (Table 3.7).

Table 3.6 Goodness of fit for the model response surface design parameters

Solution	Gas flow	Oven prog	t Fit	R_{1-2} Fit	R_{2-3} Fit	R_{3-4} Fit	Composite Desirability
Best	2.58	49.46	8.05	149.5	143.6	81.20	0.7589

Table 3.7 Validation of Predicted versus Experimental Values of Model

Response	Predicted	Experimental (n = 3)	Standard Error	% Difference
t (min)	8.05	8.28	± 0.04	2.78

The performance of the method was evaluated by conducting an external calibration. Calibration concentrations of the four standards were prepared at 20, 50, 100 and 200 µg/mL and triplicates injected for each concentration. The relative standard deviations (RSD) of the retention times (t_m) and peak areas of the four fractions were calculated. The results outlined in Table 3.8 show a good reproducibility for both the retention times as well as the areas of the peak. The calibration lines also show good linear correlation coefficients ($R^2 > 0.99$) for all the fraction standards analysed.

Table 3.8 Analytical Performance and Calibration Data of Validated Method

Fraction	RSD (%) t_m (n = 3)	RSD (%) Peak area (n = 3)	Calibration linear equation	Coefficient of regression (R^2)
C10	0.02	0.17	y =14.975x + 272.21	0.9925
C16	0.28	0.41	y = 36.774x+1812.7	0.9941
C34	0.35	1.20	y = 38.516x+1567.4	0.9905
C50	0.78	1.79	y = 9.4776x+614.68	0.9966

RSD = Relative Standard Deviation

3.3 APPLICATION OF THE OPTIMIZED METHOD FOR CONTAMINATED SOIL ANALYSIS

3.3.1 Sample Preparation of Extracted Soil Samples

The experiments focused on the chromatographic analysis of C_{10} – C_{50} (F2 –F4) fractions on the GC, since the volatile C_6 – C_{10} (F1) fractions were not present in the weathered contaminated soil whose analyses informed the need to have this CCME method developed, optimized and validated. The samples extraction method outlined in the CCME guideline [180] was followed for the C_{10} to C_{50} hydrocarbons except that in places where a mixture of 50:50 Hexane: Dichloromethane were used in instead of Toluene as specified in the guideline. Toluene was replaced because, in previous experiments where Toluene was used in the extraction process, there were no elution of the C_{34} and C_{50} (F3 and F4 fractions) in the chromatograph.

Five (5) grams of dry weight of soil was put in a tarred soxhlet thimble. A soxhlet apparatus was set up to extract the soil sample with 50:50 n-hexane:acetone at 20:1 solvent:dry soil ratio. The extraction proceeded for 16 hours with the soxhlet operating at six (6) cycles per hour. After 16 hours, the solvent was recovered and passed through 8 g of dried sodium sulphate in a column. The sodium sulphate was rinsed through with 5 mL of hexane after which 2 mL of Hexane: Dichloromethane (50:50) was added to the recovered solvent in an evaporating vessel. The solvent was then evaporated to a volume of 2 mL. An in-situ silica gel clean-up (minimum 20 mL of 50:50 Hexane:dichloromethane (DCM) was used to recover the solvent. This was followed by the addition of 3g of 100% activated silica gel to the Hexane/DCM/mixture, an amount equivalent to 0.6 g silica gel per gram of dry sample. After 5 minutes, the solvent was recovered from the mixture. 1 mL of Hexane:DCM was added to the recovered solvent in an evaporating vessel and allowed to evaporate to a volume of 1 mL. The samples were transferred to the chromatographic vials and placed on the GC sampler for immediate analysis.

3.3.2 GC-FID Experimental Conditions

The extracted samples were prepared in 90/10 (v/v) hexane/dichloromethane solvent mixture. The final optimum parameters and settings for the GC-FID analysis are: injection of 3 µL of samples in a splitless injection mode at 400 °C. The carrier gas, helium, was set at a flow rate of 2.6 mL/min. The temperature program for the oven

was as follows: the column was held at 50 °C for 0 min, ramped at 55 °C/min to 350 °C and held for 5 min. This program enabled a full analysis to be performed in 8 minutes (based on the optimized conditions), a great improvement over previously reported methods requiring about 18 to 20 minutes for the full run. A chromatogram of an extracted soil sample is shown in Figure 3.5, and the following are details of the optimized GC conditions

Table 3.9 Summary of the optimized GC Operating Conditions/Settings

GC Parameter/Condition	Optimized Setting
Column	MXT® - 1 (15m x 250 µm x 0.1µm). Max temp: 430°C
Injection Mode	Splitless
Solvent	Hexane-DCM (90:10)
Injection volume	3µL
Carrier gas	Helium
Carrier gas flow rate	2.6 mL/min.
Average velocity of the carrier gas	75.867 cm/sec.
Flow type	Constant flow
Oven program	50 °C for 0 min ramped at 55 °C/min to 350 °C, hold for 5 min
Injector temperature	400 °C
Inlet pressure	18.256 psi
Septum purge flow	3mL/minute
Purge flow split vent	70 mL/minute at 0.5 minute
Post-run total flow	25 mL/minute
Gas saver mode	On at 20 mL/min after 1 minute
Detector	Flame Ionization Detector (FID)
Detector temperature	400 °C
Hydrogen flow rate	400 mL/min
Air flow rate	450 mL/min
Make-up gas (Nitrogen) flow rate	10 mL/min

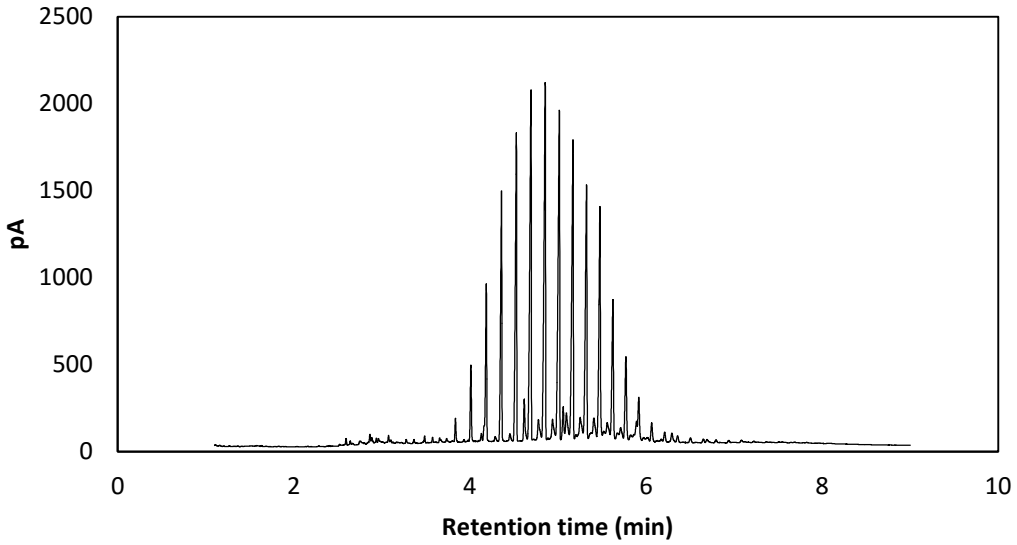

Figure 3.5 Chromatogram of TPH analyses of extracted Bunker C oil Sample

3.3.3 Evaluation of TPH concentration in Contaminated Soil

The method of calculating for the concentration of the four fractions (F1, F2, F3 and F4) was modified from the one described in the CCME reference method [180]. The standards were used as retention time markers and the total peak area evaluated for each of the fractions as shown below for F1:

$$\boldsymbol{Concentration\ of\ F1\ (C_6 - C_{10}) = \sum (A_{C6} - A_{C10}) \times F}$$

Where A_{C6} – A_{C10} refer to the sum of all areas from C_6 to C_{10} and F is the dilution factor of the sample.

The linear standard calibration equations were used to calculate the corresponding concentration of the four fractions. In addition, the solvent blank and baseline peaks were subtracted from the samples to eliminate any errors associated with contaminants in the extracted sample. The concentration found in the extracted sample is shown in Table 10. The TPH of the analysis is the sum of all the fractions together, which is 858.30 ppm. This was the total concentration (TPH) of Bunker C oil in the soil. It must be noted that the chromatogram of the C34 to C50 returned to baseline at C50, therefore not requiring the need to conduct gravimetric heavy hydrocarbon (F4G) analysis.

Table 3.10 Concentrations of TPH fractions in the Analyzed Bunker C Oil in Soil.

Fraction	Concentration (µg/mL)	Standard deviation (n = 3)	Standard Error
C_{10}-C_{16}	ND	ND	-
C_{16}-C_{34}	667.05	11.94	± 6.89
C_{34}-C_{50}	191.27	35.33	± 20.39

ND = not detected or below detection limit.

3.4 CONCLUDING REMARKS AND FUTURE WORK

It is critical that methods for analysis of contaminated sites be consistent, robust, and accurate in order to accurately assess environmental risk analysis as well as the design and evaluation of remediation process and meet regulatory guidelines/standards. In this work, we have demonstrated the application of multivariate experimental design approach for the development and optimization of a (new) GC-FID method for the

analysis of TPH in contaminated soils. The optimum GC-FID conditions obtained is this work gave a total analysis time of 8 minutes for TPH analysis compared to about 20 minutes (or more) normally required for analysing such samples. In addition, this methodology successfully captures the heavier (C_{34} – C_{50}) fractions, a feat these researchers could not achieve using the GC operating settings highlighted in the CCME guideline. The analysis time of a method is important for high throughput which is critical when a large site/region is being remediated and many samples must be analysed. The use of CCD allowed for the modelling of a second order polynomial function that was used to predict and optimize successfully the analysis time response factor. The methodology was further validated and showed a good fit. The developed method was therefore applied for the analysis of a real sample. This improvement over the current CWS-CCME standard method is expected to enable high throughput analysis of TPH with the GC-FID. As the method was tested in a single laboratory, future work of transferring the method to other laboratories and equipment will be attempted.

The authors would like to recommend the use of this method with a variety of soil types including peaty soils and heavy clay soils to further establish more confidence and reliability in the revised method. Also, future validation experiments on this method will not only be limited to Bunker C oil analysis, but will include other TPH products to represent the full C6 – C50 (F1 – F4) range, and beyond (i.e. F4G).

The effect(s) of silica gel clean-up on the analysis, and the actual quantity of silica gel per soil weight (amount of soil) to be applied based on this new conditions will be an

interesting area to study in future work, especially with this faster approach to analysing TPH with the GC-FID.

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CHAPTER FOUR

Assessment, Evaluation and Optimization of Surfactant Enhanced Soil Washing of Bunker C oil Contaminated Soil

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CO-AUTHORSHIP STATEMENT

The principal author of this paper is Abdulrazaq Zubair, who performed all the literature searches required for the background information, came up with the design of the experimental set-up, statistically designed and conducted the laboratory and analytical experiments, interpreted the results and wrote the paper. The co-authors are Dr. Lesley A. James, and Dr. Kelly Hawboldt, who provided technical guidance and edited the manuscript in their capacities as supervisors.

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ABSTRACT

Surfactant enhanced soil washing has been appraised to be an effective method for remediating a variety of hazardous substances in the soil. However, this technology has not been fully documented for Bunker C fuel oil remediation from the soil. Bunker C oil, is one of the most frequently spilled petroleum products and a highly recalcitrant compound which has been widely reported in different research to be difficult to remediate by almost all the popular remediation technologies, owing to its high fraction of heavy hydrocarbons, as well as other complicated constituents.

This paper presents an assessment; evaluation as well as experimental and statistical analyses of the main and interactive effects during the surfactant soil washing of Bunker oil impacted soil in a series of experiments designed with fractional factorial approach. Experimental factors varied were: surfactant concentrations below the CMC, washing temperature, washing time, washing speed and salinity of the washing water respectively. These parameters were chosen to provide a wide range of options for the remediation industry practitioners depending on the economic (surfactant concentration and washing duration), climatic (washing temperature) and environmental (salinity of the washing water) factors prevailing at the remedial site. The results showed that Bunker C oil can be removed from the soil with soil washing technology at surfactant concentrations below the CMC. It was also found that the behavior and reaction of surfactants differ under different conditions. A numerical

optimization method was employed in establishing predictive mathematical models for Bunker C removal for the surfactants, and the optimum Bunker C removal conditions (optimization) for the two surfactants tested

1.0 INTRODUCTION

Petroleum production, processing, transportation, storage, handling, use and disposal can result in the contamination of soils, water, and atmosphere. Soil pollution by petroleum hydrocarbons is typically a result of improper storage, handling, disposal, historic careless and accidental spills, and leakage from storage tanks [84]. Pipeline corrosion as well as blow-out from pipes and pumps [3], and everyday operations at retail outlets [4] have also been identified as sources of petroleum hydrocarbons in the environment. In some cases, deliberate disposal and discharge of oil and oily wastes to the environment could be a major cause of this environmental damage [5]. Contamination of soil impacts flora, fauna and is a potential risk to human health [34]; limiting the soil use for agricultural purposes; threatening the safety of potable water, limiting the use of groundwater and causing enormous economic loss and ecological disaster [28]. Data from the federal contaminated site inventory indicate that there are over 30,000 m^3 of brownfield sites across Canada [2]. These are sites that have been previously used for industrial and commercial activities and have been contaminated with hazardous wastes. It is therefore, imperative develop remediation technologies that are economically and scientifically feasible, fast, and applicable in a wide range of physical settings.

The most common hydrocarbon contaminants include; crude oil, gasoline, diesel, polychlorinated biphenyls (PCB), polyaromatic hydrocarbons (PAH), Bunker C, engine oil,

etc. Bunker C fuel oil [7]; is referred to as a recalcitrant compound in that it is persistent (resistant to chemical and biological degradation) and therefore difficult to remediate [8]. It is a complex petroleum mixture derived from residuals of refinery processing [8]. It is the heaviest of fuel oils [8], and contains high concentrations of *n*-C_{12} through *n*-C_{34} alkanes [86], and appreciable quantities of polycyclic aromatic hydrocarbons (PAHs), with concentrations of four to six ring condensed PAHs representing 5 % or more of the total mass [6]. Furthermore, Bunker C oil contains elevated levels of sulfur (1.5 – 4 wt.%) [87]. These high fraction of heavy hydrocarbons and other complicated constituents translates to a low water solubility (complicating removal by water based treatment processes), low volatility (limiting thermal treatment), and low biodegradability (resistance to microbial breakdown), leading to its continued persistence in the environment. Bunker C is widely used around the world, in marine fuel for shipping [87, 90], and also used in oil fired power generation, and at remote site locations like mine sites [40]. It is one of the most frequently spilled petroleum products in the US [8] and known to be more toxic than other petroleum oils because of its high PAH content [90].

When Bunker C spills into the environment, due to its complex chemical composition [8, 87], it weathers slowly and can persist relatively unchanged for years [90, 92]. The ecological effects of Bunker C spillage are enormous. Ingestion of low concentrations is associated with reproductive failures [93], genotoxicity [94], and hematological changes [95, 96] in different animals. Environmentally, its elevated sulfur content generates serious air pollution during combustion due to SOx emission [97], while its PAHs content

makes it a potential cancer causing contaminant, because many PAHs are carcinogens [98] and immunotoxins [99].

Over the past years, concerted efforts have been geared towards the remediation of Bunker C with the use of well-known remedial processes, most of which have been reported to be unsuccessful by many researchers. Song et al. [31], studied the microbial degradation of terrestrial fuels (gasoline, jet fuel, heating oil, diesel oil and Bunker C) in different soils. The research reported that the degradation of Bunker C from the soil was very slow and incomplete, as none of the Bunker C treated soils reached a 50 % reduction after 48 weeks of treatment. According to their results, bioremediation initially accelerated Bunker C degradation, but no further stimulation was recorded after 8 weeks. The study suggested that Bunker C components were structurally resistant to biodegradation, and concluded that bioremediation has only very limited beneficial effects remediation from the soil. These results confirmed the findings of Walker et al [100], which had earlier reported Bunker C to be the least susceptible oil to biodegradation. Richmond et al. [8] experimented the optimization of emulsification and biodegradability of Bunker C oil from the soil and reported an 8 % mineralization of Bunker C after 6 weeks of treatment, and also noted the toxicity of the oil to the microbes. In a similar research, Floodgate, [101] stated that when Bunker C spills, its high viscosity leads to the formation of tar balls, that can physically isolate a bulk of the oil from microbial degradation and dispersion. The tarry consistency of Bunker C, as reported by Irwin et al., [6] makes it difficult to be remediated from the contaminated

surfaces. The National Oceanic and Atmospheric Administration (NOAA) [102] reported Bunker C to be difficult to remove from oiled surfaces, and relatively recalcitrant to biodegradation [8]. It is also reported to be the least susceptible fuel oil to biodegradation [100]; and very slow, incomplete and structurally resistant to bioremediation [31]. According to the NOAA report [102], Bunker C weathers very slowly, chemical dispersion is seldom effective, and clean-up is difficult under all conditions. From the foregoing, Richmond et. al. [8], concluded that current remediation strategies are inadequate and a need exists for research aimed at improving our ability to clean-up past and future spills of Bunker C.

This study assessed the performance of surfactant enhanced soil washing remediation technology, simply known as soil washing, for the remediation of Bunker C contaminated soil. It is a technology that involves high energy contact between contaminated soils and an aqueous based washing solution, resulting in the separation of hazardous materials and/or the chemical transformation of contaminants into non-hazardous, unregulated substances [49]. It primarily utilizes liquids, usually water, combined with surfactants, and mechanical processes to scrub contaminated soils [16] and proposed as a possible remediation option for soils contaminated by petroleum hydrocarbons and other hydrophobic organic chemicals [47]. It is very effective in removing a mixture of contaminants such as heavy metals, pesticides and herbicides as well as other hazardous and non-degradable substances from contaminated soils and water in a one step process [83]. Soil washing is easy to implement, efficient,

economical, environmentally friendly [52], cost effective, relatively fast, and has the potential to treat and recover large volumes of contaminants [53]. It also requires less time than biological methods, and can be used for both in-situ and ex-situ methods [55]. Soil washing relies on the use of surfactant formulations to target organic and inorganic contaminants from soil and sediments by selectively desorbing them from solid to liquid phase [51]. Surfactants are surface-active compounds act by reducing surface and interfacial tensions at the interphases between liquids, solids and gasses [107]. When present at low concentration in a system, surfactants adsorb onto the surfaces or interfaces and alter the surface or interfacial free energies of those surfaces or interfaces [103]. They are the active ingredients found in soaps and detergents, and are commonly used to separate oily materials from a particular media [42]. Surfactants exist as monomers, which can aggregate with increased concentration to form micelles at a concentration known as the Critical Micelle Concentration (CMC) [103]. Surfactants remove contaminants via two type of mechanisms; one occurs below the CMC known as soil rollup or mobilization mechanism, and the other above the CMC known as solubilization [108]. The roll up mechanism is effective in remediating many contaminants [129, 130], is cost efficient, and compatible with analytical testing procedures [52]. Solubilization involves washing at higher surfactant concentration, above the CMC, which usually increases the cost of remediation, and problematic due to colloid mobilization [131], clay swelling [132] and macro-emulsion formation [133].

Studies on soil washing of Bunker C contaminated soil are not very common. Contaminants such as; crude oil, TPH, engine oil, diesel etc. [56-61], heavy metals [45, 46, 49, 62-64], PCBs [41, 65, 66], wood preservatives [67], PAH [66, 68, 69], phenanthrene [70], pesticides [71, 72] and a mixture of contaminants [49] have been successfully remediated using SESW. It is also worth noting that this technology has been widely adopted in cleaning up superfund sites in the USA [73]. However, it has not been widely reported for the remediation of Bunker C impacted soil. This study analyzes the effects of soil washing parameters on the removal of Bunker C oil from weathered contaminated soil with patented non-ionic surfactants, and developed a model to optimize parameters for Bunker C oil remediation with surfactants, using the multivariate experimental design approach.

Multivariate approaches can be used to study the relationships between responses and a number of (numerical and categorical) variables, such that the optimal settings for the variables to obtain maximum or minimum response levels can be identified and validated. The traditional method of examining a single factor at a time (one factor at a time) for optimization of multivariable systems are extremely time-consuming, expensive, and does not consider the interactive effects between different experimental parameters therefore, cannot determine the practical optimum conditions [197-200]. A more effective approach therefore is the utilization of a multivariate experimental design, where statistical data is used as an optimization tool. One of these methods is the design of experiment (DOE) approach which is used in this study, which offers

essential information about the optimization process by indicating the individual, synergistic interactive and/or antagonistic effects of each experimental factor [199] considered.

Multivariate experimental approaches for optimization soil washing of hydrocarbon compounds have been reported in the literature [42, 145, 198, 200], however none on the optimization of soil washing of Bunker C fuel oil from soil. The goal of this study was to evaluate the usability of soil washing technology for Bunker C fuel oil remediation from contaminated soil. More specifically, to assess the performance of two different patented non-ionic surfactants for Bunker C soil washing, and investigate the effects of the soil washing and environmental parameters on the process. Finally, the study seek to find the optimum soil washing removal conditions for Bunker C oil with the non-ionic surfactants; Iveysol® 106 and Iveysol® 108 formulations respectively. In achieving all these, the study was conducted in different phases.

4.1 METHODOLOGY

The first phase (Section 4.3.1) involves the evaluation of the Bunker C removal efficiency of the surfactants with five (5) different soil washing parameters in a set of experiments designed with a two-level fractional factorial design (*f*FD). The experimental parameters varied were: surfactant concentrations (% vol/vol), washing temperature (^{o}C), washing speed (rpm), salinity of the washing water (ppt), and washing time (minutes). These experiments gave an insight into the significant factors and how the interactive

significant factors, where found, can be best combined to achieve maximum Bunker C removal with each surfactant. It also provides feasibility on how much of Bunker C oil in-terms of Total Petroleum Hydrocarbon (TPH) can be removed through soil washing.

In the second phase (Section 4.3.2), the data generated were subjected to a multi-factor numerical and predictive model to find the optimum Bunker C removal condition with each surfactant. The numerical optimization concept utilizes predictive models to maximize, minimize or target a single or combination of responses that are subjected to upper and/or lower boundaries to construct desirability indices, otherwise known as desirability function. This method is increasingly becoming a popular form of optimizing multiple factors to find the optimal contaminant removal condition in remediation studies. For instance, Kalali et al., [200] used a similar approach to optimize hydrocarbon-polluted soil remediation. Currently, there are no optimization studies that focus on using soil washing for the remediation of Bunker C oil from weathered contaminated soil. A set of numerical mathematical models were also generated for each of the surfactant tested.

The model predicted conditions were later verified and validated (Section 4.3.4) in a series of experiments repeated three times for each surfactant under similar conditions. The results of these validation experiments were compared with those predicted by the model and the difference (in percentage) was highlighted.

4.2 MATERIALS AND METHODS

4.2.1 Soil Samples

Weathered soil samples contaminated with Bunker C oil obtained from an old mining site was used for this study. Weathered soils are known to be more difficult to remediate than newly contaminated soils [32, 69, 74, 75], as weathering processes such as evaporation and degradation concentrate contaminants and increases their molecular weight, viscosity and density, as well as enhances the binding strength of oil to the soil. Mass transfer rates of hydrophobic organic compounds (HOCs) are also known to be small in weathered soils [75]. Therefore, weathered contaminated soils, which this study utilized, are usually much more difficult to remediate than recently contaminated soils [32].

Preliminary analyses are necessary to understand the kind of soil we were dealing with. Particle size analysis was conducted to determine the percentage of sand, silt, clay and coarse materials in the soil. Particle size distribution determines the suitability of the soil for soil washing, as soil washing is not considered to be effective when soils contain more than 20 - 30% silt/clay [35, 134, 201]. Upon analysis, the soil was found to be made up of 10.7 % silt, 40.5 % sand, 7.2 % clay, and 41.6 % coarse-grained sediments respectively. The bulk density was 1.4 g/cm^3, moisture content 11 % and the pH was 7.85

4.2.2 Surfactants and other Reagents

The non-ionic surfactants used, Iveysol® 106 and Iveysol® 108 surfactant formulations were obtained in kind from Ivey International Inc., BC, Canada. The CMC of the surfactants, as reported as reported from our previous study [202] (Chapter two) were determined using Laser Scanning Drop Shape Analysis (LASDA) tensiometer and found to be 0.029 %v/v for Iveysol® 106 and 0.020 %v/v for Iveysol® 108 . Deionized water and seawater whose salinity were measured as 0 ppt and 33 ppt respectively were used as washing solvents for the soil washing process carried out in a variable speed (89.7 – 517 rpm) batch mixer. A 0.5 mm sieve and a VWR analog shaker (Figure 1) were used for rinsing the soil after washing.

4.2.3 Experimental Design and Parameters

Five different quantitative factors, namely: surfactant concentrations, (washing) temperature, salinity of the washing water (deionized and seawater), washing speed, and washing time were selected for this study. In this first phase, evaluation of Bunker C removal efficiency was investigated in a set of experiments designed with a 2-level fractional factorial analysis, with minimum resolution five (5^{-1}) and three centre points, using the Design Expert® 9.0 software. This kind of design is a fraction of a full factorial design that confounds some main effects with interactions or interactions among themselves, resulting in a smaller set of experiments, and, nevertheless, able to identify the influence of each parameter, as well as first-order interactions between factors

[203]. It also allow the effects of a factor to be estimated at several levels of the other factors, yielding conclusions that are valid over a range of experimental conditions [88].

Typically, in 2-level fractional factorial designs, the number of experiments are expressed as J^{k-1}, where J is the number of levels tested and *k* is the number of factors [203-205]. To check the occurrence of curvature, three centre points were added. The experiment was therefore designed with the five variable factors at high and low levels (2^{5-1}) and three (3) centre points to produce 19 experiments per surfactant, with the targeted response being the TPH presented as the percentage of Bunker C removed by each surfactant. Thereafter, significant factors were identified and the interactive factors were discussed. The experimental factors and the level which they were investigated are shown in Table 4.1.

Table 4.1 Factors and their levels used in the Fractional Factorial Design

Effects	Code	Units	-1	0	+1
Surfactant Concentration	A	% Vol/Vol	-0.9*	-0.7*	-0.5*
Temperature	B	^{o}C	5.0	22.5	40.0
Salinity of Water	C	ppt	0.0	16.5	33.0
Washing Time	D	min	1	3	5
Washing Speed	E	rpm	89.7	135.7	181.7

* Surfactant concentrations at 90, 70 and 50 % below the CMC

In the second phase, the data generated from the fractional factorial experiments were analysed using the Design Expert® 9.0 software and quadratic models that allows for the assessment of predicted response (Y) as a function of the independent and interactive variables were developed for each surfactant. An analysis of the variance (ANOVA) was conducted to assess the goodness and validity of the models generated using the Fischer trial (F-test) and probability value (t-test) at 95 % confidence level. Finally, the optimal values of the tested variables were obtained from numerical optimization; a multi-factor optimization tool which searches the design space, using the models created during analysis to find factor settings that meet the defined goals. The optimal values were then validated in a series of replicated soil washing experiments, and the model and experimental results were compared.

4.2.4 Washing Process

The experimental set-up is shown in Figure 4.1. The experiments were conducted in a high power variable speed batch mixer placed in a temperature controlled incubator in a series of steps enumerated as thus:

800g of contaminated soils was collected using a simple random sampling technique and weighed into the batch mixer. Surfactants were diluted to 50 % and 90 % below their respective CMCs using deionized and sea water respectively. A one litre (1 L) of surfactant solution and the 800 g soil were warmed to experimental temperature in the incubator. Once the specified experimental temperature was reached, the surfactant

and the soil were mixed together at the specified speeds for the specified mixing time in the incubator. *Samples* were taken at 1 minute and 5 minutes, depending on the time allotted to the experimental run. The washed soil were allowed settle for approximately 5 minutes until the soil settled below the petri dish, and the washed solution was decanted. Rinsing of the washed soil was done with two liters of water (either seawater or deionized water, depending on the type of water used in preparing the surfactant solution) on a 0.5 mm sieve placed on a shaker. The sieve was continuously vibrated on a shaker for approximately 1 minute. The rinsed soil samples were transferred into 65 mL sampling bottle with no head-space, kept at -35 ^{o}C until it was ready for pre-analysis sample extraction.

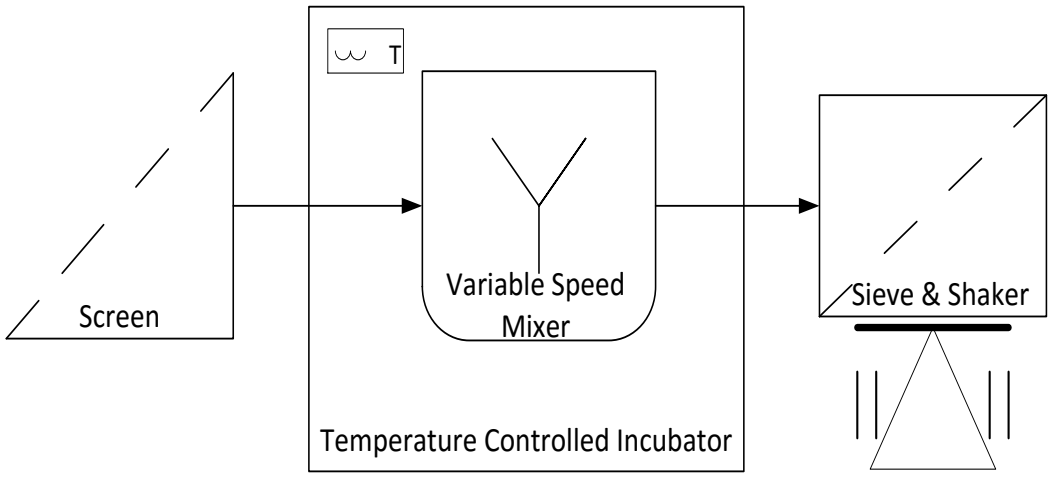


Figure 4.1 Schematic Illustration of the Experimental Set-up with the Batch Mixer

4.2.5 Laboratory Analyses

Analyses of the pre and post washing soils were carried out using the modified and optimized version of Canada Wide Standard (CWS) method analyses of Petroleum Hydrocarbon (PHC) in soil which was fully reported in our previous study [206] (shown in Chapter three of this thesis). The Canada Wide Standard is a remedial standard for contaminated soil and subsoil grounded in the science of risk assessment [179]. Sequel to the soxhlet extraction of the Bunker C oil from the soil, the sample were analyzed based on the fractions of the hydrocarbon i.e. F1 (C_6-C_{10}), F2 (C_{10}-C_{16}), F3 (C_{16}-C_{34}), F4 (C_{34}-C_{50}) and F4G-sg (Gravimetric Heavy Hydrocarbons), and the sum of these hydrocarbon fractions represents the total hydrocarbon in the soil before and after washing.

The percentage of Bunker C oil removed was determined using the equation below:

$$\text{Bunker C oil removed} = \frac{(B_i - B_f)}{B_i} \text{ x } 100\% \qquad (1)$$

Where B_i is the initial concentration of Bunker C oil in the soil, and B_f is the final Bunker C concentration in the soil after washing. Table 4.2 gives the experimental layout and the percentage of oil removed from the soil with each surfactant. This gives inkling to the maximum percentage of Bunker C oil removed with each of the surfactants in set of experiments which involved simultaneous combination of factors. The responses were

coded as Y_1 and Y_2 to generate mathematical models that expresses the behavior of Iveysol® 106 and Iveyso® 108 surfactants with Bunker C removal.

4.3 RESULTS AND DISCUSSION

4.3.1 Fractional Factorial Experiments

The goals of the phase was to assess the possibility of remediating Bunker C oil with surfactant soil washing, and identify the factors and combination of factors that may have significant effects on Bunker C removal with this process Table 4.2 shows the effects of the selected experimental parameters on Bunker C oil removal (TPH) at each experimental run. The data were analyzed using Pareto Chart tool to identify and gain an understanding of the magnitude and the significance of each parameter. The Pareto Chart is a dimensionless statistical tool which scales the effects of experimental parameters in terms of standard deviations with it vertical axis representing the t-value of the absolute effects [205]. Any experimental factor(s) that is above the t-limit value (horizontal) line in the Pareto chart is considered to be significant factor(s) at 95% confidence level. Studies such as Pandey et al., [194], Puertas et al., [195] etc. made use of the Pareto charts to select the significant factors in their experiments. Upon analysis, some interactive (combined) factors were found to be significant along with single factors. The Model Graph Tool, another Design Expert® tool, was used to statistically evaluate the interactions of the combined interactive significant factors, and how best

to combine those factors under different conditions to achieve maximum Bunker C oil removal.

Table 4.2 FFD Experimental Matrix and Percentage of Bunker C oil Removed

	Experimental Factors					% Removal of Bunker C oil	
Run	**A**	**B**	**C**	**D**	**E**	**106**	**108**
1	1	1	1	-1	-1	71.9	58.5
2	1	-1	1	1	-1	63.5	64.6
3	0	0	0	0	0	89.7	70.2
4	1	-1	-1	-1	-1	80.8	88.1
5	0	0	0	0	0	84.4	70.2
6	1	1	1	1	1	85.1	85.5
7	-1	-1	-1	1	-1	74.2	96.9
8	-1	1	1	-1	1	87.3	88.9
9	-1	-1	1	-1	-1	85.3	61.3
10	-1	1	1	1	-1	82.1	69.3
11	-1	-1	1	1	1	90.9	79.1
12	0	0	0	0	0	77.0	70.9
13	-1	1	-1	1	1	90.9	96.9
14	1	-1	1	-1	1	77.0	61.3
15	1	-1	-1	1	1	88.9	72
16	-1	1	-1	-1	-1	90.1	84.8
17	-1	-1	-1	-1	1	94	75.9
18	1	1	-1	1	-1	92.8	76
19	1	1	-1	-1	1	91.9	72.3

A = Concentration; B = Temperature; C = Salinity; D = washing Time; E = Washing Speed

4.3.1.1 Iveysol® 106 Surfactant Formulation

As shown in the Pareto Chart for Iveysol® 106 (Figure 4.2), the significant factors with this surfactant are Washing Speed (E), Salinity (C), and the interaction of Concentration and Salinity (AC). These are the factors that were above the t-value limit at 95% confidence level.

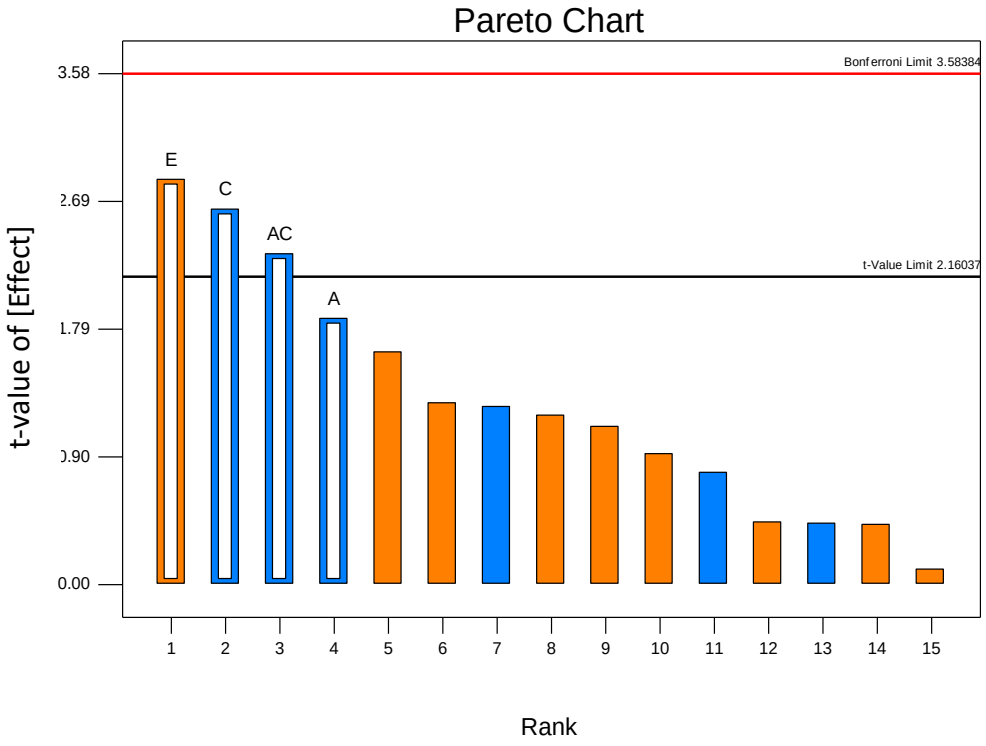
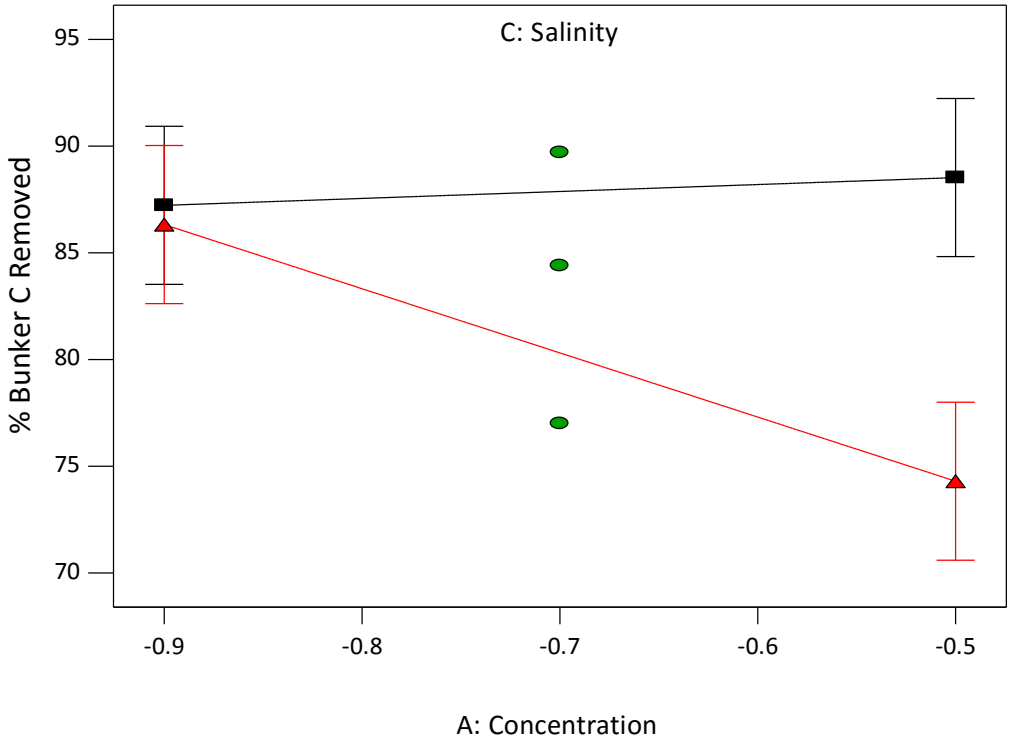


Figure 4.2 Pareto Chart for Iveysol® 106

The interaction of surfactant concentration and salinity (AC) shown in Figure 4.3, is the only significant interactive factor for Iveysol® 106. At low and high surfactant concentrations, the use of fresh deionized water for Bunker C soil washing led to higher

Bunker C oil removal, removing 87.9 % Bunker C at low surfactant concentration (90 % below the CMC) and 89.1 % at high surfactant concentration (50 % below the CMC). For the saline seawater, washing at low surfactant concentration (90 % below the CMC) is more beneficial as it removed more Bunker C oil than at high surfactant concentration (90 % below the CMC).



-0.9 = below the CMC, -0.7 = 70% below the CMC

Figure 4.3 Interaction of Surfactant Concentration (A) with Salinity (C) for Iveysol® 106

4.3.1.2 Iveysol 108® Surfactant Formulation

As shown in Figure 4.4, surfactant concentration (A), salinity (C), washing time (D), and the interactions of salinity with washing speed (CE) and washing temperature with washing speed (BE) are the significant effects with Iveysol® 108 surfactant.

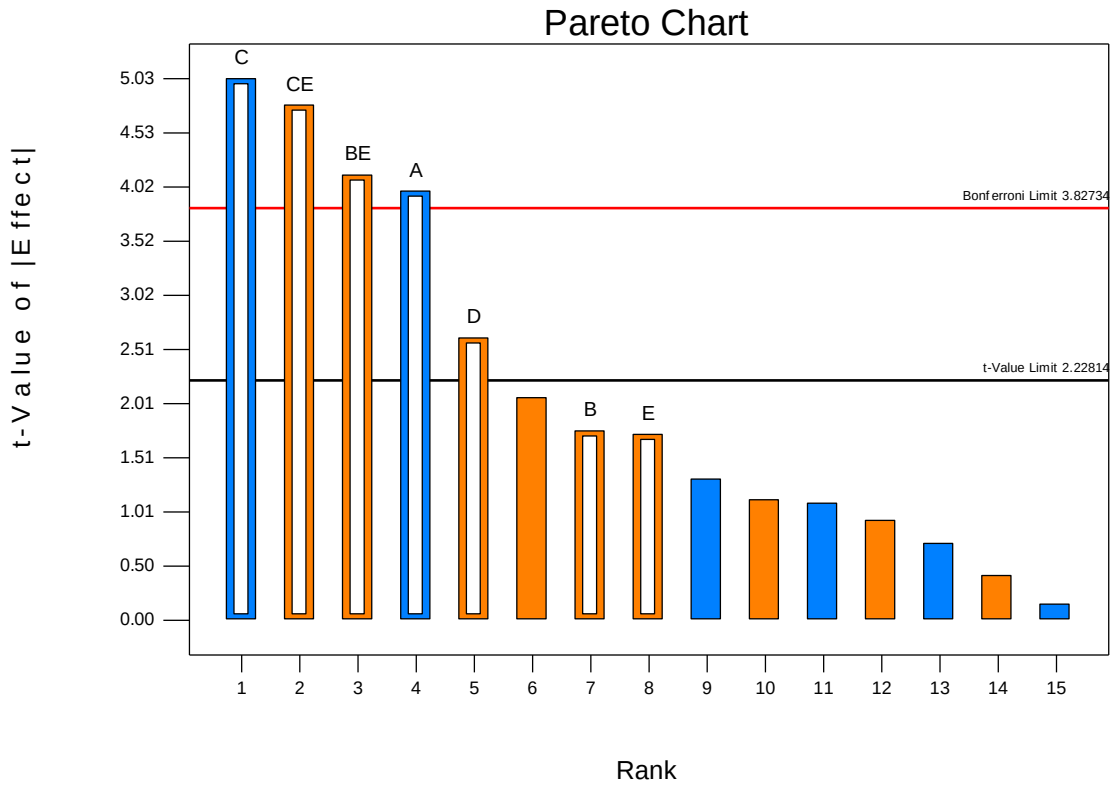


Figure 4.4 Pareto Chart for Iveysol® 108

The interactions between washing temperature and speed (BE) with respect to Iveysol® 108 are presented in Figure 4.5. Washing Bunker C contaminated soil at high washing speed (181.70 rpm) and high temperature (40 ^{0}C) with this surfactant favors higher

Bunker C oil removal (84.8 %) than washing at the same speed but at low temperature (5 ^{0}C). This higher Bunker C removal was as a result of the synergistic effects of these two important factors (temperature and mixing speed). At high temperature, hydrocarbon molecules generally become more mobile due to reduced viscosity; therefore, this enabled the Bunker C molecules to desorb from the soil surface. This effect of high temperature on hydrocarbon removal during soil washing agrees with the results of other studies such as Urum *et.* al, 2005a [57], Urum *et.* al, 2005b [58] and Zhang *et*. al. [207]. Therefore, washing at high temperature and at high mixing (washing) speed or agitation rate will lead to increased Bunker C oil removal.

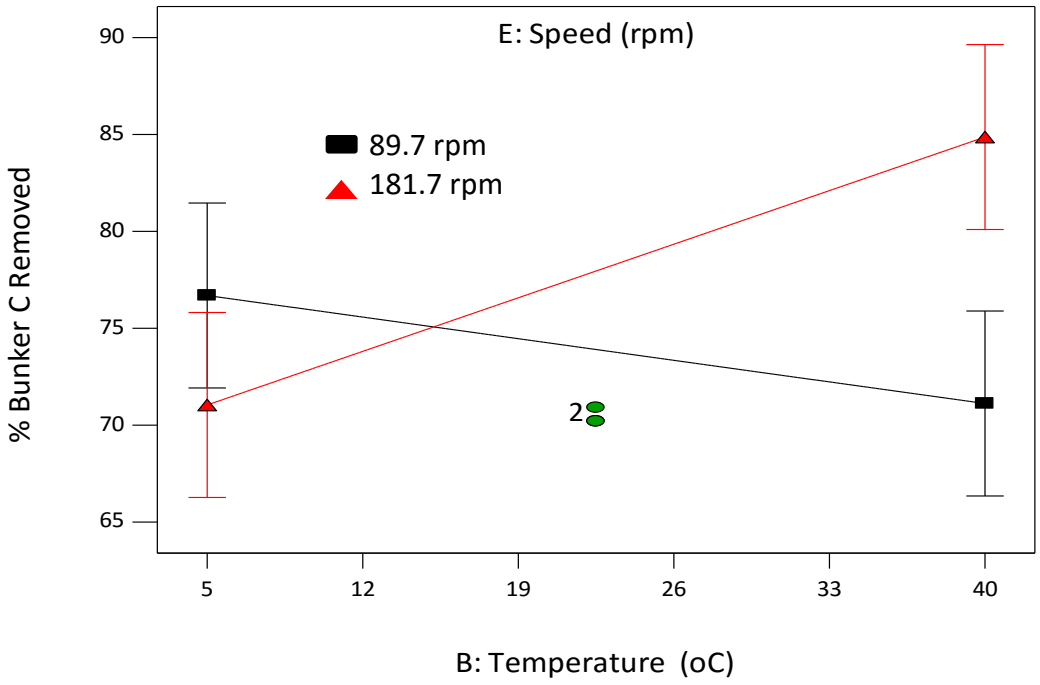


Figure 4.5 Interactions of Temperature (B) and Speed (E) with Iveysol 108®

Looking at the interaction between Salinity and Washing Speed (CE) shown in Figure 4.6, high washing speed of 181.7 rpm leads to high Bunker C oil removal regardless of the washing solvent (deionized water or seawater), with deionized water (0 ppt), 78.2 % of the Bunker C oil was removed, while a total of 77.6 % Bunker of the C oil removal was recorded with the saline seawater (33 ppt). This indicates that the high washing (mixing) speed provided the needed energy to break the forces attraction and adsorption binding the Bunker C molecules to the surface of the weathered contaminated soil regardless of the salinity of the washing solvent.

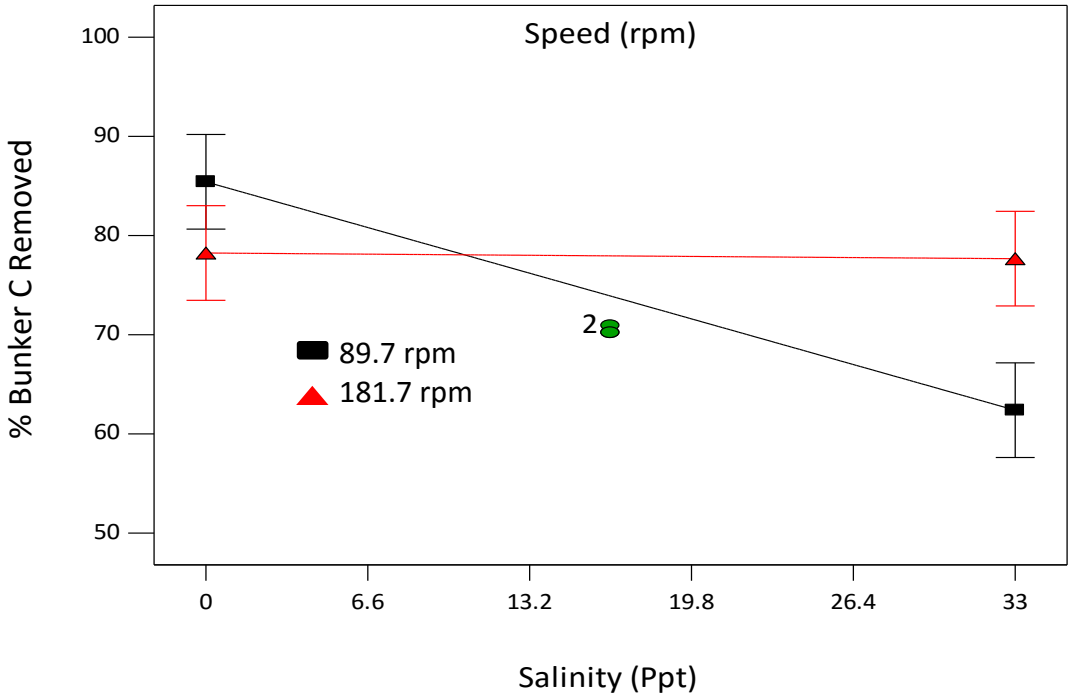


Figure 4.6 Interactions of Salinity and Washing Speed (CE) with Iveysol 108®

Washing Bunker C contaminated soil at high washing and mixing speed, also exposed more surface area of the soil to the Iveysol® 108 surfactant solution thereby ensuring effective mobilization, displacement and desorption of the oil from the solid (soil surface) phase to the liquid phase (washed solution). This is in agreement with the findings Urum *et. al* [57], who investigated the effects of washing parameters on six (6) different biosurfactants during the soil washing of crude oil contaminated soil.

Washing at a low washing speed (89.70 rpm) however, removed more Bunker C oil with freshwater water (85.4 % removal) compared to washing with seawater, where it removed an only a 62.3 % Bunker C oil. In summary, the table below gives a quick view of the significant parameters for each surfactant tested.

Table 4.3 Significant (operating) Factors for the Surfactants

Surfactant	Significant Factors (Parameters)				
Iveysol 106	Salinity	Speed		Concentration-Salinity	
Iveysol 108	Concentration	Salinity	Speed	Concentration-Time	Temperature-Time

4.3.2 Optimization Experiments

In this (second) phase, the data generated from the fractional factorial experiments were analysed and the models for the total petroleum hydrocarbon (PH) removed after

soil washing (as a function of the independent and interactive experimental variables) were developed for the surfactants. An analysis of variance (ANOVA) was conducted to assess the robustness of the models with the F-test and t-test at 95 % confidence level.

The models generated from ANOVA analyses in terms of actual factors for the Iveysol surfactants are:

$$Y_{106} = 78.11 + 3.25\mathrm{A} - 0.935\mathrm{C} + 0.089\mathrm{E} - 0.100\mathrm{AC} \quad (2)$$

$$Y_{108} = 87.18 - 23.38\,\mathrm{A} - 0.699\mathrm{B} - 1.361\mathrm{C} + 1.538\mathrm{E} + 0.00602\mathrm{BE} + 0.00739\mathrm{CE} \quad (3)$$

Y_{106} and Y_{108} are the predicted Bunker C oil removal (TPH) by Iveysol® 106 and Iveysol® 108 in percentage.

The fitness of each model was evaluated. For Iveysol® 106, the model is significant at F-value of 6.42, and there is only a 0.38 % chance that a "Model F-Value" this large could occur due to noise (Table 4.4). Generally, values of "Prob > F" less than 0.0500 indicate model terms are significant. In this case, salinity (C), time (E), and the interaction of concentration and salinity (AC) were the significant model terms.

The "Lack of Fit F-value" of 0.71 implies the Lack of Fit is not significant relative to the pure error. Therefore, there is a 71.67 % chance that a "Lack of Fit F-value" this large

could occur due to noise. A non-significant lack of fit is statistically desired, as it indicates the fitness of the model. Prior to arriving at the Anova analysis in Table 4.4, the model was refined. It will be noted that despite not being significant in the Pareto chart in Figure 4.2, surfactant concentration (A), appears as a significant effect in the Anova Table (Table 4.4) and the model equation (equation 2). This is based on the regression assumption that even though surfactant concentration (A) is not very significant at P-value 0.0732 (which is greater than 0.05), it is less than 0.100, therefore, it was assumed or considered to be significant. Also, a combination of surfactant concentration and salinity (AC) is a very significant factor, if surfactant concentration (A) is removed, AC becomes insignificant (Appendix A4) hence, it was left in the model equation.

Table 4.4 ANOVA for selected factorial model for Iveysol® 106

	Sum of		Mean	F	p-value	
Source	**Squares**	**df**	**Square**	**Value**	**Prob > F**	
Model	787.85	4	196.96	6.42	0.0038	significant
A-Concentration	115.03	1	115.03	3.75	0.0732	
C-Salinity	228.77	1	228.77	7.46	0.0162	
E-Speed	266.51	1	266.51	8.69	0.0106	
AC	177.56	1	177.56	5.79	0.0305	
Residual	429.26	14	30.66			
Lack of Fit	347.88	12	28.99	0.71	0.7167	not significant
Pure Error	81.38	2	40.69			
Cor Total	1217.11	18				

For Iveysol® 108; although lack of fit exists, the model is significant at an F-value of 9.93 with 0.05 % chance that an F-value of such magnitude could occur. The significant model terms were surfactant concentration (A), salinity (C) the combined interactions of temperature with time (BE), and that of salinity with time (CE). Therefore, there were two significant main variables (A and C), and two interactive variables (BE and CE). If there are many significant models (parameters), as seen in this case, the model can still be used [208], even if the lack of fit is significant. Based on this, the study proceeded on using the model. The models were refined and two assumptions were made. Firstly, although temperature (B) is not an independently significant factor, it was used in the modelling equation for Iveysol® 108 (Equation 3) and it is included in the model (Table 4.5). This is because, although temperature (B) presented a P value of 0.1590 which was greater than 0.100, and therefore, is not significant, but a combination of Temperature and Speed (BE) presents a very significant term at P-value of 0.0045. Therefore, Temperature (B) is assumed to play an important role in the performance of Iveysol® 108 formulation.

The second assumption made was to include washing speed (E) in the model, due to the effect it has on another significant term CE (Salinity and Speed), in which, although E was not a significant term on its own (P-value = 0.1660), removing it from the model may greatly affect CE. It was therefore, assumed to be a significant term and added to the model.

Table 4.5 ANOVA for selected factorial model for Iveysol 108®

	Sum of		Mean	F	p-value	
Source	**Squares**	**df**	**Square**	**Value**	**Prob > F**	
Model	2071.98	7	296.00	9.93	0.0005	**significant**
A-Concentration	349.69	1	349.69	11.73	0.0057	
B-Temperature	68.06	1	68.06	2.28	0.1590	
C-Salinity	556.96	1	556.96	18.68	0.0012	
D-Time	151.29	1	151.29	5.07	0.0457	
E-Speed	65.61	1	65.61	2.20	0.1660	
CE	504.00	1	504.00	16.91	0.0017	
Residual	327.95	11	36.40			
Lack of Fit	327.62	9	0.16	222.87	0.0045	**significant**
Pure Error	0.33	2				
Cor Total	2399.92	18				

Based on the models, a numerical optimization of the surfactants was performed to obtain the optimal values of the tested variables for each surfactant. The optimization is a multi-factor optimization method; a tool which searches the design space, using the models created to find factor settings that meet the defined goals. In numerical optimization, goals can be assigned or selected for targeted response in lower and upper limits. The possible goals are: maximize, minimize, target, within range, none (for responses only) and set to an exact value (factors only). The Design Expert® software enables the allocation of a minimum and a maximum level for each experimental variable (parameter). A weight can also be assigned to each goal to adjust the shape of

its particular desirability function. This value can range from 0.10 to 10 and it fine-tunes how the optimization process searches for the best solution. A low weight (near 0.10) will allow more solutions that don't quite meet the optimal goal, while a high weight (close to 10) will cause the optimization to seek a solution close to or beyond the stated goal. Table 4.6 give the optimization criteria settings used for the optimization of the process, while the optimum experimental conditions obtained for the two surfactants are presented in ramps shown in Figures 4.7 and 4.8.

Table 4.6 Optimization Criteria Settings

Surfactant	Response Factor	Goal	Target	Minimum	Maximum	Weight
Iveysol 106	% Bunker C removal	Target	99 %	90 %	100 %	1
Iveysol 108	% Bunker C removal	Target	99 %	90 %	100 %	1

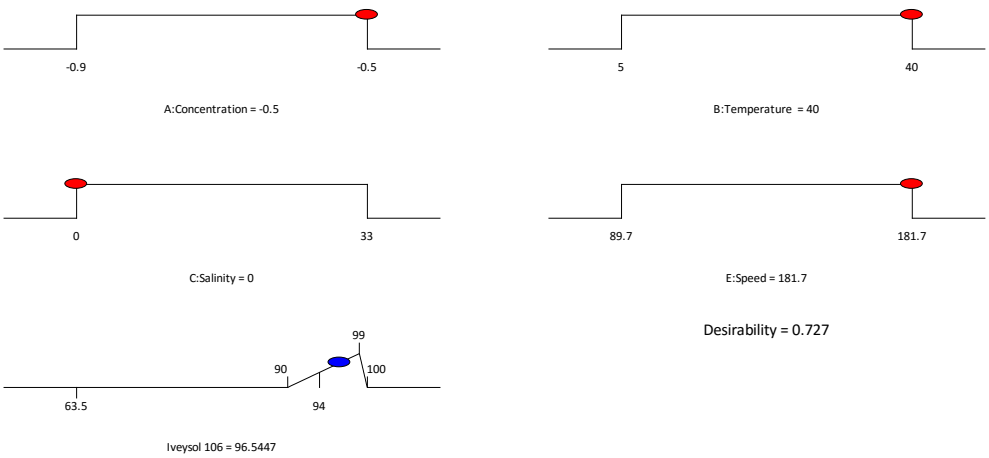


Figure 4.7 Optimization Ramps for Iveysol® 106 Surfactant

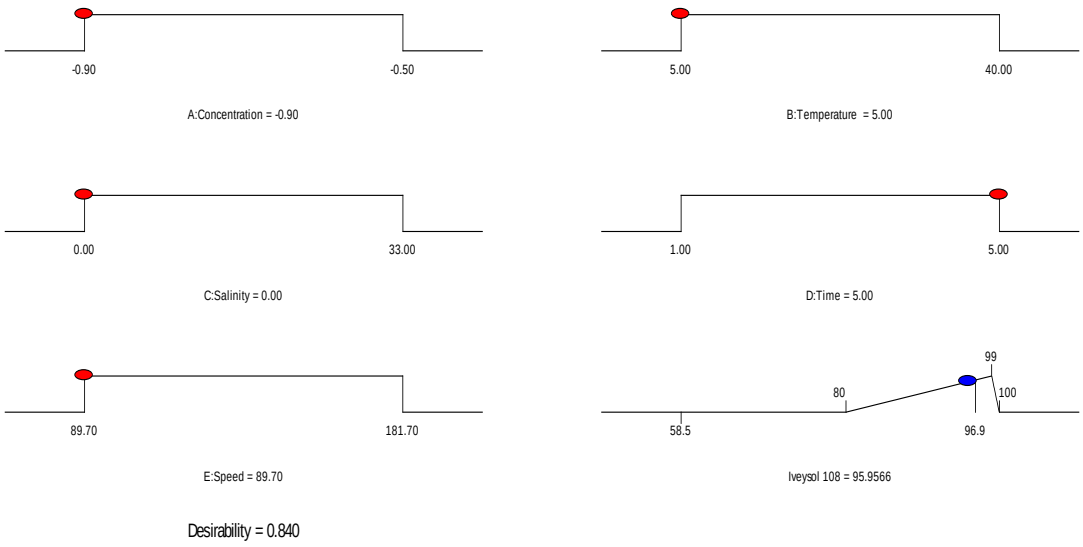


Figure 4.8 Optimization Ramps for Iveysol® 108 Surfactant

Ramps are a graphical view of each optimal solution for easier interpretation. Optimal factor settings are shown with red dots, while the optimal expected response values are displayed in blue. The height of the dots shows how desirable they are, and the over-all desirability score is also displayed. From the ramp, an optimum Bunker C removal of 96.5 % was predicted for Iveysol® 106 surfactant via a combination of high surfactant concentration (50 % below the CMC), high temperature (40 ^{o}C), washing with deionized water (salinity of 0 ppt), at high washing speed (181.7 rpm) for a duration of 1 minute. Iveysol® 108 had a combination of low surfactant concentration (90 % below the CMC), low temperature (5 ^{o}C), with deionized water (salinity of 0 ppt) and at low washing

speed (89.7 rpm), to remove 92.88 % of Bunker C oil from the soil. Both Iveysol® 106 and 108 surfactants showed an acceptable desirability of 0.727 and 0.840 respectively. Desirability ranges from zero to one for any given response. The Design Expert software® combines individual desirabilities (of each factor) into a single overall desirability factor. A value of 1.0 represents an ideal case; a value close to 1.0 is acceptable, while zero (0) indicates that one or more responses fall outside the desirability limits. It was based on these predicted optimal conditions that the validated experiments were executed.

4.3.3 Model Validation Experiments

To validate the optimum process conditions for the two surfactants, soil washing experiments were conducted at the experimental levels shown in the ramp figures (4.7 and 4.8). In order to observe the effect of noise during the washing process, each experiment was repeated three times (n = 3) under the same conditions at different times, and the average percentage Bunker C removed is recorded as the TPH remediated after the process. Table 4.7 shows the results of the validation experiment compared favorably with the predicted model data with 10.3 % and 3.5 % difference for Iveysol® 106 and Iveysol® 108 respectively.

Table 4.7 Predicted and Experimental Results for Iveysols 106 and 108

Surfactant	Model Prediction	Experimental (n=3)	% Difference
Iveysol® 106	96.5 %	86.6 %	10.3 %
Iveysol® 108	92.8 %	96.1 %	3.5 %

5.0 SUMMARY, RECOMMENDATIONS AND CONCLUSIONS

Utilizing the fractional factorial design (fFD) enabled us to conduct minimum number of experiments with limited available field-contaminated soil samples at our disposal to see the effects of the parameters on each surfactant and cofound those independent and interactive effects in a smaller set of experiments. Bunker C fuel oil, an otherwise recalcitrant contaminant reported to be difficult to remediate through many remediation technologies is indeed possible to remediate through surfactant enhanced soil washing process at surfactant concentration below the CMC (roll-up mechanism). Surfactant washing at concentrations below the CMC, as earlier highlighted, is cost effective [52], does not cause colloid mobilization [131], clay swelling [132] and macro-emulsion formation [133], unlike washing at surfactant concentration above the CMC (mobilization mechanism). It is worth noting that these studies were conducted with real (not simulated) weathered contaminated soil, shown in the literature to be very difficult to remediate [69, 74, 75]. More precisely, the two surfactants used; Iveysol 106 and Iveysol 108, both removed a maximum of 96.9 % and 94.0 % of Bunker C oil

respectively, prior to finding the optimal conditions. This is a significant feat and a goal of every field remediation project.

The selection of optimum operational parameters in soil washing is critical. The parameters selected for this study are known to have affected the washing of other hydrocarbon compounds in the soil. These parameters were chosen at levels that are likely to affect contaminant removal in a soil-contaminant-surfactant system, and/or based on prevailing weather conditions (low and high temperature), capacity of soil washing equipment (washing speed), as well as available resources (clean or saline water) close to a remediation facility/site. All these were done with the aim to identify which parameters or combinations of parameters (interactions) are significant for each surfactant, and how their combination (interaction) would lead to maximum Bunker C removal – in the case of interactive parameters. The variations in the performance of each surfactant indicate the behavior and reaction of surfactants to the washing parameters or conditions are different validating the importance of the methodology developed in this work. In their screening experiments, Deshpande et al., [108] had also noted a wide variation in the behavior of the tested surfactants to the experimental parameters and in the overall oil removal and indicated the importance of bench top experiments prior to large scale application for new surfactant-contaminant systems. We have developed a method and model which could be used to reduce the number of bench top experiments and optimize process conditions. This will enable operators to

decide which surfactant to use, and which parameters to combine when washing at low and high temperature season (washing temperature), in an environment with abundant freshwater or seawater (salinity), and whether to execute the washing at high or low agitation rate (washing/mixing speed). Although, economic considerations will dictate the preferred surfactant to be selected for a washing operation.

One of the challenges faced in this research was the limited amount of Bunker C contaminated soil. Ideally further experiments would have been conducted with Iveysol® 108, whose model had a significant lack of fit, which is often not desirable statistically, but due to lack of abundant soil samples, more experiments could not be conducted to fill the linearity, even though the model is acceptable. However, the models optimum conditions were tested and validated.

Since soil washing is a phase-transfer process in which contaminants are transferred from the solid (soil surface) to the liquid phase (waste water), the management and treatment of the desorbed contaminant (in the effluent) generated after the washing, remains a serious and expensive challenge for the remediation industry. Toxicity testing on the effluent will be recommended to ascertain how much of the oil got transferred to the water phase. This study will also further recommend studies on the treatment and possibly, recovery of the Bunker C oil and the surfactant from the effluent.

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CHAPTER FIVE

RESEARCH SUMMARY, RECCOMENDATIONS AND CONCLUSIONS

Bunker C oil pollution, and indeed, soil pollution due to spillage and mishandling of hydrocarbon compounds is a global phenomenon, and one of the biggest challenges threatening the continued preservation, conservation, and sustenance of the natural environment. Bunker C fuel oil pollution most especially, is a very big problem, owing to its predominant use in the marine industry, and for power and heat generation at remote site locations.

The literature reviewed outlined the various challenges of existing remediation technologies in successfully remediating Bunker C fuel oil in the soil. Surfactant enhanced soil washing technology is an effective at remediating all kinds of contaminants and a mixture of contaminants from the soil. This study investigated and developed a surfactant soil washing process for Bunker C oil remediation that meets economic and environmental requirements, through the soil mobilization (roll up mechanism), which entails using the minimum concentration (amount) of surfactants at concentrations below the surfactants CMC.

One of the objectives of this research was to investigate the CMC of the Iveysol surfactants, which although, have been widely used for all kinds of remediation

activities but no study exists on their CMC values. Chapter two focused on the use of Pendant Drop and Tensiometery methods for the determination of the CMC of Iveysol surfactants. The challenges in determining accurate CMC values and reasons why it is preferable to use different methods to determine CMC were addressed.

In determining the efficacy and efficiency of soil washing on Bunker C remediation, it was imperative to reliably quantify the concentration of Bunker C oil in terms of Total Petroleum Hydrocarbon (TPH) in the soil. The study sought to validate the Canada Wide Standard (CWS) method on the GC-FID, which is Canada's approved method for the analyses of hydrocarbons in the soil. After a series of trial, it was found that there were some inadequacies in the chromatographic conditions stipulated in the method. This has significant repercussions in determining baseline contamination and most effective remediation strategies and therefore the method was modified. In chapter three, the method was modified, optimized and validated to obtain a more reproducible, accurate and faster method than the previous Canada Wide Standard (CWS) method. This method can be adopted by commercial laboratories and regulatory agencies to develop better remediation approaches to heavy hydrocarbon contamination.

The main objective of this study was to determine the usability of soil washing in removing Bunker C oil from the soil. The literature surveyed revealed there was no existing study related to the protocols involved in soil washing of Bunker C soil. Also, extensive study on optimization of soil washing parameters for maximum Bunker C

removal have not been reported. All these were investigated in chapter four, by firstly using the fractional factorial designed (FFD) methodology to design soil washing experiments to evaluate Bunker C removal at surfactant concentrations below the CMc. The results of the two surfactants tested had at least 90 % Bunker C removal.

The use of multivariate experimental approach afforded us the opportunity highlight the effects of the selected experimental parameters as well as interactive effects of combined significant parameters on the overall Bunker C removal efficiency. Also, the optimum operational parameters which can be combined, and how they can be combined to ensure a successful Bunker C removal with soil washing were revealed and discussed. The parameters selected and the levels at which they were used was based on the premise of their likelihood to affect a soil-contaminant-surfactant system, and based on weather conditions that might be prevailing at a remediation site, and/or the available resources or equipment at the disposal of the soil washing company. Another significant achievement of this study was the use of site-contaminated and not laboratory simulated contaminated soil. As highlighted in the literature survey in Chapter one, weathered field contaminated soils are more difficult to remediate and very recalcitrant to remedial treatment. Therefore, the use of weathered contaminated soils provided the needed confidence in the results.

Chapter four also touched on the variations in the performance, behavior and reaction of each surfactant to the experimented parameter, which was one of the significant

objectives of this work, as various researchers had in the past enumerated that these differences indeed occur on the basis of contaminant and surfactant type.

The predictive and optimization conditions generated were tested, validated and found to fall within statistically acceptable limit, thereby justifying the essence of the entire work and how industry practitioners can effectively utilize the predicted models, and the suggested combination of factors for their day to day Bunker C remedial operations.

In summary, the novelty in this study is the development of a soil washing protocol, methodology and a practical approach for remediating Bunker C and other heavy oil with surfactants enhanced soil washing. The novelty lie in the step by step approach it enumerated in executing soil washing with surfactants (Chapter 4, section 4.2.4), and most importantly, it developed a robust analytical method for analyzing hydrocarbon in the soil. It is worth noting that this study is the first academic thesis on the use of soil washing for Bunker C oil remediation. It must also be stated that the utility of the findings of this work is not limited to only Iveysol surfactants, as it serves as a template for the use of soil washing with different surfactants for Bunker C clean-up.

The approach to soil washing outlined in this work will enable operators to decide which surfactant to use, and which parameters to combine when washing in the at low and high temperature season (washing temperature), in an environment with abundant freshwater or seawater (salinity), and whether to execute the washing at high or low

agitation (washing/mixing speed), but most importantly, economic considerations will dictate the preferred surfactant to be selected for a washing operation.

The research would recommend inter-laboratory investigation of the analytical method developed, as this will further provide more confidence in the method and ensure repeatability and reproducibility of the method with entirely different GC-FID, under the same chromatographic conditions. The use of the method with a variety of soil types including peaty soils and heavy clay soils to further establish more confidence and reliability in the revised method will also be highly recommended. Also, future validation experiments on this method should not only be limited to Bunker C oil analysis, but should include other TPH products to represent the full C6 – C50 (F1 – F4) range, and beyond (i.e. F4G). The effect(s) of silica gel clean-up on the analysis, and the actual quantity of silica gel per soil weight (amount of soil) to be applied based on this new conditions will be an interesting area to study in future work, especially with this faster approach to analyzing TPH with the GC-FID.

The greatest challenge faced in this research, as earlier enumerated in the concluding section of Chapter four was the limited amount of Bunker C contaminated soil. Ideally further experiments would have been conducted with Iveysol 108, whose model had a significant lack of fit, which is often not desirable statistically, but due to lack of abundant soil samples, more experiments could not be conducted to fill the linearity, even though the model is acceptable. However, the models optimum conditions were

tested and validated. Therefore, a more statistically evaluated further studies will be very beneficial. The research will also recommend further studies on the effect of surfactants, and overall soil washing process on the (mechanical and hydraulic) properties of the treated soil. Another limitation of the work was the inability to give comprehensive chemistry of the surfactants utilized, which made it difficult to explain the chemistry and interfacial phenomena behind the behaviors and reactions of the surfactants.

Another great limitation with this work was the non-usage of other commercial surfactants to compare their chemistry, properties, and Bunker C removal efficiency with that of the Iveysol surfactants.

Since soil washing is a phase-transfer process in which contaminants are transferred from the solid (soil surface) to the liquid phase (waste water), the management and treatment of the desorbed contaminant (in the effluent) generated after the washing, remains a serious and expensive challenge for the remediation industry. Toxicity testing on the effluent will be recommended to ascertain how much of the oil got transferred to the water phase. This study also recommends further studies into the treatment and possibly, recovery of the Bunker C oil and the surfactants from the effluents.

APPENDIXES

APPENDIX A1: CALIBRATION OF THE TENSIOMETER

The calibration of the tensiometer as per instruction manual was according to the following procedure:

A small strip of paper was placed on the ring of the tensiometer (Figure 2.1) to serve as a platform. The lever arm was released and the knurled knob (A) was turned until the index (I) was brought in line with its mirror image and exactly in line with the reference line on the mirror. The dial clamp (C) was loosened and dial (S) was rotated until the Vernier (V) indicated approximately zero on the dial. The fine adjustment screw (F) was rotated until the Vernier scale reads exactly zero.

A mass of 0.636 g was placed on the paper platform and the knurled knob (A) was turned until the index (I) was opposite the reference line on the mirror. The dial reading was recorded to the nearest 0.10 division and the dial reading was confirmed using the equation:

$$P = \frac{Mg}{2L} \qquad (1)$$

where:

M = weight placed on ring = 0.636 g

g = value of gravity = 980.3 cm/s^2

L = mean circumference of the ring = 6.17 cm

P = dial reading = apparent surface tension in dynes.cm^{-2}

$$P = (0.636\ g \times 980.3\ cm/s^2) / (2 \times 6.17\ cm) = 50.52\ dynes.cm^{-1}$$

The calculated value (50.52 dynes/cm^{-1}) was equal to the adjusted reading, hence the calibration was correct. If the recorded dial reading is greater than the calculated value by 0.5 dynes.cm^{-2}, the adjustment nut (G) would be adjusted to shorten the lever arm; if the dial reading is less than the calculated value by 0.5 dynes.cm^{-1}, the nut (G) would be been adjusted to lengthen the arm.

Having calibrated the tensiometer correctly, each unit on the dial represents a surface or interfacial tension of exactly 1 dyne/cm$^{-1.}$

APPENDIX A2: SURFACE TENSION MEASUREMENT WITH THE TENSIOMETER METHOD FOR TRITION X-100

Surfactant Concentration	1st Measurement (Dynes/cm)	2nd Measurement (Dynes/cm)	Average Surface Tension (dynes/cm)	Average Surface Tension (N/M)	Ln C	STDV
0.050	53.2	52.8	53.0	0.053	-3.0	0.3
0.100	37.8	36.7	37.3	0.037	-2.3	0.8
0.125	34.5	35.9	35.2	0.035	-2.1	1.0
0.250	30.5	30.0	30.3	0.030	-1.4	0.4
0.500	29.8	30.0	29.9	0.030	-0.7	0.1
0.750	30.0	30.0	30.0	0.030	-0.3	0.0
1.000	30.0	30.0	30.0	0.030	0.0	0.0

STDV = Standard Deviation

APPENDIX A3: SURFACE TENSION MEASUREMENT WITH THE TENSIOMETER METHOD FOR IVEYSOL 106

Surfactant Concentration	1st Measurement (Dynes/cm)	2nd Measurement (Dynes/cm)	Average Surface Tension (dynes/cm)	Average Surface Tension (N/M)	Ln C	STDV
0.005	51.9	50.9	51.4	0.051	-5.3	0.7
0.010	43.3	43.9	43.6	0.044	-4.6	0.4
0.025	34.3	35.0	34.7	0.035	-3.7	0.5
0.050	34.2	35.6	34.9	0.035	-3.0	1.0
0.075	34.7	34.8	34.8	0.035	-2.6	0.1
0.100	35.3	34.5	34.9	0.035	-2.3	0.6
0.250	34.6	34.7	34.7	0.035	-1.4	0.1

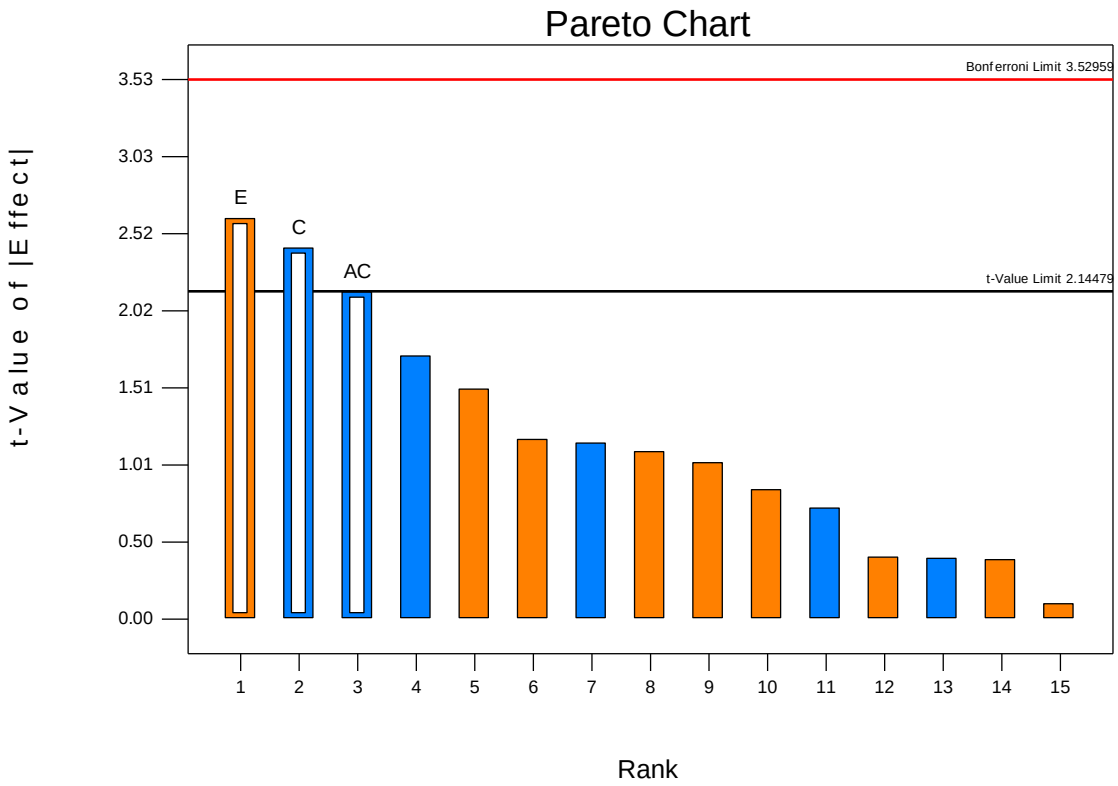
STDV = Standard Deviation

APPENDIX A4: SURFACE TENSION MEASUREMENT WITH THE TENSIOMETER METHOD FOR IVEYSOL 108

Surfactant Concentration	1st Measurement (Dynes/cm)	2nd Measurement (Dynes/cm)	Average Surface Tension (dynes/cm)	Average Surface Tension (N/M)	Ln C	STDV
0.005	32.0	34.2	33.1	0.033	-5.3	1.6
0.010	32.7	32.5	32.6	0.033	-4.6	0.1
0.025	30.0	32.6	31.3	0.031	-3.7	1.8
0.050	30.1	32.5	31.3	0.031	-3.0	1.7
0.075	30.0	32.1	31.1	0.031	-2.6	1.5
0.100	31.6	30.9	31.3	0.031	-2.3	0.5
0.250	31.0	31.4	31.2	0.031	-1.4	0.3

STDV = Standard Deviation

APPENDIX A5: PARETO CHART FOR IVEYSOL 106 WITH SURFACTANT CONCENTRATION (A) REMOVED FROM THE MODEL



APPENDIX A6: METALS IN THE CONTAMINATED SOIL

Metal	Concentration (ppm)	CSQG (ppm)
Chromium (VI)	31.9	1.4
Zinc	87.9	360.0
Lead	49.2	600.0
Cadmium	1.4	22.0
Arsenic	5.7	12.0
Mercury	-0.03	300.0
Copper	31.1	91.0
Nickel	16.58	50.0
Antimony	40.0	1.5
Silver	0.4	40.0
Selenium	-5.7	2.9

CSQG = Canadian Soil Quality Guideline

APPENDIX A7 DATA FOR CMC MEASUREMENT BY THE TENSIOMETRY METHOD

CMC Measurement for Iveysol® 103

Concentration	Suface Tension 1	Surface Tension 2	Average Surface Tension (dynes/cm)	Average Surface Tension (N/m)	ln C
0.005	34.5	35.5	35.0	0.0350	-5.30
0.010	34.8	34.0	34.4	0.0344	-4.61
0.025	32.8	32.0	32.4	0.0324	-3.69
0.050	30.5	30.0	30.3	0.0303	-3.00
0.075	30.9	30.8	30.9	0.0309	-2.59
0.100	31.0	30.5	30.8	0.0308	-2.30
0.250	29.5	29.7	29.6	0.0296	-1.39
0.500	31.0	29.4	30.2	0.0302	-0.69
0.750	30.5	28.2	29.4	0.0294	-0.29
1.000	30.0	30.1	30.1	0.0301	0.00

CMC Measurement for Iveysol® 106

Concentration	Surface Tension 1	Surface Tension 2	Average Surface Tension (dynes/cm)	Average Surface Tension (N/m)	ln C
0.005	51.9	50.9	51.4	0.051	-5.3
0.010	43.3	43.9	43.6	0.044	-4.6
0.025	34.3	35.0	34.7	0.035	-3.7
0.050	34.2	35.6	34.9	0.035	-3.0
0.075	34.7	34.8	34.8	0.035	-2.6
0.100	35.3	34.5	34.9	0.035	-2.3
0.250	34.6	34.7	34.7	0.035	-1.4
0.500	34.5	34.8	34.7	0.035	-0.7
0.750	34.6	34.2	34.4	0.034	-0.3
1.000	34.6	34.2	34.4	0.034	0.0

CMC Measurement for Iveysol® 108

Concentration	Surface Tension 1	Surface Tension 2	Average Surface Tension (dynes/cm)	Average Surface Tension (N/m)	ln C
0.005	32.0	34.2	33.1	0.033	-5.3
0.010	32.7	32.5	32.6	0.033	-4.6
0.025	30.0	32.6	31.3	0.031	-3.7
0.050	30.1	32.5	31.3	0.031	-3.0
0.075	30.0	32.1	31.1	0.031	-2.6
0.100	31.6	30.9	31.3	0.031	-2.3
0.250	31.0	31.4	31.2	0.031	-1.4
0.500	31.1	31.3	31.2	0.031	-0.7
0.750	31.1	31.3	31.2	0.031	-0.3
1.000	31.3	31.1	31.2	0.031	0.0

CMC Measurement for Triton X-100

Concentration	Suface Tension 1	Surface Tension 2	Average Surface Tension (dynes/cm)	Average Surface Tension (N/M)	ln C
0.050	53.2	52.8	53.0	0.053	-3.0
0.100	37.8	36.7	37.3	0.037	-2.3
0.125	34.5	35.9	35.2	0.035	-2.1
0.250	30.5	30.0	30.3	0.030	-1.4
0.500	29.8	30.0	29.9	0.030	-0.7
0.750	30.0	30.0	30.0	0.030	-0.3
1.000	30.0	30.0	30.0	0.030	0.0

APPENDIX A8 DATA FOR CMC MEASUREMENT BY THE PENDANT DROP TECHNIQUE

CMC Measurement for Iveysol® 103

Concentration (%vol/vol)	Equilibrium Surface Tension	ln C
0.0016	0.0475	-6.43775
0.004	0.0393	-5.52146
0.006	0.0350	-5.116
0.008	0.0318	-4.82831
0.012	0.0286	-4.42285
0.02	0.0280	-3.91202
0.03	0.0278	-3.50656
0.3	0.0279	-1.20397
3	0.0279	1.098612

CMC Measurement for Iveysol® 106

Concentration (%vol/vol)	Equilibrium surface Tension (N/m)	ln C
0.006	0.04338	-5.116
0.0075	0.04285	-4.89285
0.009	0.04001	-4.71053
0.012	0.03791	-4.42285
0.025	0.0339	-3.68888
0.03	0.03279	-3.50656
0.04	0.032543	-3.21888
0.06	0.03243	-2.81341
0.3	0.03241	-1.20397

CMC Measurement for Iveysol® 108

Concentration (%vol/vol)	Equilibrium surface Tension (N/m)	ln C
0.006	0.03761	-5.116
0.008	0.03488	-4.82831
0.01	0.03411	-4.60517
0.012	0.03182	-4.42285
0.015	0.03064	-4.19971
0.02	0.02816	-3.91202
0.025	0.02816	-3.68888
0.04	0.02806	-3.21888
0.08	0.028051	-2.52573
0.8	0.02799	-0.22314